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Daniel Treadwell

RUMFORD PROFESSOR AND LECTURER
ON THE APPLICATION OF SCIENCE
TO THE USEFUL ARTS
1834–1845

TEXT-BOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., F.R.S.

TEXT-BOOKS OF PHYSICAL CHEMISTRY.

EDITED BY SIR WILLIAM RAMSAY, K.C.B., F.R.S.

THE progress of Physical Chemistry is now so rapid, its domain is so extensive, and the number of journals devoted to its exposition is so great, that it has appeared desirable to issue a series of volumes, each of moderate compass, and each dealing with one branch of the subject. The rate of advance in various branches of the subject is not equal; while, for example, the basis of the science remains comparatively stationary (for methods of determining atomic and molecular weights, and the classification of compounds undergoes little modification), rapid progress is being made in other branches Hence it has been thought proper to issue several short manuals, so that each individual one may be frequently brought up to date, independently of others. In this way, a statement of what is known on each subject will be made accessible to students and investigators. The subject ha been divided as follows, among the authors mentioned:—

AN INTRODUCTION TO PHYSICAL CHEMISTRY. By SIR WILLIAM RAMSAY, K.C.B., F.R.S. 1*s.* net.[1]

THE PHASE RULE. ALEXANDER FINDLAY, D.SC. 5*s.*

STOICHIOMETRY. PROFESSOR SYDNEY YOUNG, D.SC., F.R.S.

THE RELATION BETWEEN CHEMICAL CONSTITUTION AND PHYSICAL PROPERTIES. SAMUE SMILES, D.SC.

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CHEMICAL DYNAMICS, AND REACTIONS. J. W MELLOR, D.SC.

The order in which these parts will be issued is not that given; for some subjects are more easily treated of than others; but it is hoped that all the volumes will be ready for the press before December, 1904.

---

[1] This is the General Introduction to the series, and it also appears in Mr. Findlay's book on the Phase Rule.

THE PHASE RULE

AND ITS APPLICATIONS

BY

ALEX. FINDLAY, M.A., PH.D., D.SC.
LECTURER AND DEMONSTRATOR IN CHEMISTRY, UNIVERSITY OF BIRMINGHAM

WITH ONE HUNDRED AND EIGHTEEN FIGURES IN THE TEXT

TOGETHER WITH

AN INTRODUCTION

TO THE

STUDY OF PHYSICAL CHEMISTRY

BY

SIR WILLIAM RAMSAY, K.C.B., F.R.S.
Editor of the Series

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25 MAY 1912

DEDICATED

TO

FRANCIS ROBERT JAPP, LL.D., F.R.S.

PROFESSOR OF CHEMISTRY, UNIVERSITY OF ABERDEEN,

IN GRATITUDE FOR EARLY TRAINING

AND ADVICE

PREFACE

ALTHOUGH we are indebted to the late Professor Willard Gibbs for the first enunciation of the Phase Rule, it was not till 1887 that its practical applicability to the study of Chemical Equilibria was made apparent. In that year Roozeboom disclosed the great generalization, which for upwards of ten years had remained hidden and unknown save to a very few, by stripping from it the garb of abstract Mathematics in which it had been clothed by its first discoverer. The Phase Rule was thus made generally accessible; and its adoption by Roozeboom as the basis of classification of the different cases of chemical equilibrium then known established its value, not only as a means of co-ordinating the large number of isolated cases of equilibrium and of giving a deeper insight into the relationships existing between the different systems, but also as a guide in the investigation of unknown systems.

While the revelation of the principle embedded in the Phase Rule is primarily due to Roozeboom, it should not be forgotten that, some years previously, van't Hoff, in ignorance of the work of Willard Gibbs, had enunciated his "law of the incompatibility of condensed systems," which in some respects coincides with the Phase Rule; and it is only owing to the more general applicability of the latter that the very important generalization of van't Hoff has been somewhat lost sight of.

The exposition of the Phase Rule and its applications given in the following pages has been made entirely non-mathematical, the desire having been to explain as clearly as possible the principles underlying the Phase Rule, and to illustrate their application to the classification and investigation of equilibria, by means of a number of cases actually studied. While it has been sought to make the treatment sufficiently elementary to be understood by the student just commencing the study of chemical equilibria, an attempt has been made to advance his knowledge to such a stage as to enable him to study with profit the larger works on the subject, and to follow with intelligence the course of investigation in this department of Physical Chemistry. It is also hoped that the volume may be of use, not only to the student of Physical Chemistry, or of the other branches of that science, but also to the student of Metallurgy and of Geology, for whom an acquaintance with at least the principles of the Phase Rule is becoming increasingly important.

In writing the following account of the Phase Rule, it is scarcely necessary to say that I have been greatly indebted to the larger works on Chemical Equilibria by Ostwald ("Lehrbuch"), Roozeboom ("Die Heterogenen Gleichgewichte"), and Bancroft ("The Phase Rule"); and in the case of the first-named, to the inspiration also of personal teaching. My indebtedness to these and other authors I have indicated in the following pages.

In conclusion, I would express my thanks to Sir William Ramsay, whose guidance and counsel have been constantly at my disposal; and to my colleagues, Dr. T. Slater Price and Dr. A. McKenzie, for their friendly criticism and advice. To Messrs. J. N. Friend, M.Sc., and W. E. S. Turner, B.Sc., I am also indebted for their assistance in reading the proof-sheets.

A. F.

November, 1903.

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INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

To define exactly the provinces of the Sciences of Physics and Chemistry is not easy. The definition that the object of Chemistry is the study of the changes which matter undergoes during the formation and decomposition of compounds, while that of Physics has reference to changes which affect matter independently of its composition, hardly meets the case. It is true that it is possible to deduce certain laws relating to the properties of matter, which are valid irrespective of the chemical composition of the matter; but such laws deal with the behaviour of matter in motion, or acted on by gravitational or other forces which apply only to matter in bulk. For example, Newton's law of "gravitation"—that two masses approach each other as if impelled by a force which varies directly as their masses, and inversely as the square of the distance which separates them—takes no cognizance of the nature of the matter which attracts: the law is not affected by the chemical composition of the acting bodies. Similarly, the laws dealing with inertia are true, whatever the nature of the matter to which these laws apply. But when phenomena relating to change of volume by pressure, to the surface phenomena of liquids, to electricity, to heat, light, and other forms of wave-motion, are considered, the laws deduced from them contain specific

constants, so that their numerical application can be made only when these specific constants are known. Thus although the same differential equation governs the flow of heat in all kinds of matter, it contains a specific constant, viz. the "conductivity;" and as this varies for different kinds of matter, the chemical nature of the substance becomes a factor in the problem.

The birth of physical chemistry may be said to date from the recognition of this fundamental idea; where the laws or generalizations regarding properties of matter depend not merely on the masses or rates of motion of the objects considered, but also on their composition and chemical nature their consideration falls under the heading "Physica Chemistry."

It was not until the middle of the nineteenth century that this began to be recognized; although many facts had been discovered, and many laws deduced before that date, physical chemistry was not differentiated from physics, on the one hand, and chemistry on the other, until the dependence of certain physical phenomena on the chemical composition of the objects under consideration had become obvious.

The attempts of the ancients to interpret the facts around them led to little of value. For long mankind was contented to observe certain phenomena, and to utilize them for industrial purposes, if they were found suitable. Yet in all ages "philosophers," or lovers of wisdom, as they liked to call themselves, have endeavoured to "explain" certain observed facts. This word "explain" is frequently used without any very definite view of its signification. It may be defined as "to state the unknown in terms of the known," and this process was facilitated by grouping observed facts into similars and dissimilars The "properties of matter," for example, were "explained" by the Greeks and their predecessors by the theory that all matter partook of the nature of fire, air, earth, and water—the so-called "elements"—in greater or less proportion. But this

—more correctly *equivalents*—of the elements of which they are composed. It is to him that we owe most of our analytical methods, for prior to his time there were few, if any, accurate analyses. Although Lavoisier had devised a method for the analysis of compounds of carbon, viz. by burning the organic compounds in an atmosphere of oxygen contained in a bell-jar over mercury, and measuring the volume of carbon dioxide produced, as well as that of the residual oxygen, Berzelius achieved the same result more exactly and more expeditiously by heating the substance, mixed with potassium chlorate and sodium chloride, and thus estimating the hydrogen as well as the carbon. This process was perfected by Liebig. Berzelius, however, was able to show that compounds of carbon, like those of other elements, are instances of combination in constant and multiple proportions.

In 1815 two papers were published in the *Annals of Philosophy* by Dr. Prout, which have had much influence on the progress of chemistry. They dealt with the figures which were being obtained by Thomson, Berzelius, and others, at that time supposed to represent the "atomic weights" of the elements. Prout's hypothesis, based on only a few numbers, was that the atomic weights were multiples of that of hydrogen, taken as unity. There was much discussion regarding this assertion at the time, but as it was contradicted by Berzelius's numbers, the balance of opinion was against it. But about the year 1840 Dumas discovered an error in the number (12·12) given by Berzelius as the atomic weight of carbon; and with his collaborator, Stas, he undertook the redetermination of the atomic weights of the commoner elements—for example, carbon, oxygen, chlorine, and calcium. This line of research was subsequently pursued alone by Stas, whose name will always be remembered for the precision and accuracy of his experiments. At first Stas inclined to the view that Prout's hypothesis was a just one; but it was completely disproved by

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—more correctly *equivalents*—of the elements of which they are composed. It is to him that we owe most of our analytical methods, for prior to his time there were few, if any, accurate analyses. Although Lavoisier had devised a method for the analysis of compounds of carbon, viz. by burning the organic compounds in an atmosphere of oxygen contained in a bell-jar over mercury, and measuring the volume of carbon dioxide produced, as well as that of the residual oxygen, Berzelius achieved the same result more exactly and more expeditiously by heating the substance, mixed with potassium chlorate and sodium chloride, and thus estimating the hydrogen as well as the carbon. This process was perfected by Liebig. Berzelius, however, was able to show that compounds of carbon, like those of other elements, are instances of combination in constant and multiple proportions.

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his own subsequent work, as well as by that of numerous other observers. It is, nevertheless, curious that a much larger proportion of the atomic weights approximate to whole numbers than would be foretold by the doctrine of chances; and perhaps the last has not been heard of Prout's hypothesis, although in its original crude form it is no longer worthy of credence.

To Dalton the smallest portions of matter, whether consisting of single atoms, as that of oxygen, O, or of compounds, such as water, to which he ascribed the composition HO, were alike regarded as atoms. This view, however, conflicted with experimental data arrived at by Gay-Lussac in the year 1808. In conjunction with Humboldt, Gay-Lussac had rediscovered about three years before what had previously been established by Cavendish, namely, that, as nearly as possible, two volumes of hydrogen combine with one volume of oxygen to form water, the gases having been measured at the same temperature and pressure. Humboldt suggested to Gay-Lussac that it would be well to investigate whether similar simple relations obtain between the volumes of other gaseous substances when they combine with each other. This turned out to be the case; it appeared that almost exactly two volumes of carbonic oxide combine with one volume of oxygen to form two volumes of carbonic acid gas; that equal volumes of hydrogen and chlorine unite to form hydrochloric acid gas; that two volumes of ammonia consist of one volume of nitrogen in union with three volumes of hydrogen, and so on. From such facts Gay-Lussac was led to make the statement that the weights of equal volumes of gases, whether simple or compound, and therefore their densities, are proportional to their empirically found combining or atomic weights, or to rational multiples of the latter. Gay-Lussac regarded this discovery of his to be a support for the atomic theory, but it did not accord with many of the then received atomic weights.

The assumption that equal volumes of gases contain equal numbers of particles, or, as they were termed by him, *molécules intégrantes*, was made in 1811 by Avogadro, Professor of Physics at Turin. This theory, which has proved of the utmost importance to the sciences of both chemistry and physics, had no doubt occurred to Gay-Lussac, but had been rejected by him for the following reasons: A certain volume of hydrogen, say 1 cubic centimeter, may be supposed to contain the same number of particles (atoms) as an equal volume of chlorine. Now, these two gases unite in equal volumes. The deduction appears so far quite legitimate that 1 atom of hydrogen has combined with 1 atom of chlorine. But the resulting gas occupies 2 cubic centimeters, and must therefore contain the same number of particles of hydrogen chloride, the compound of the two elements, as 1 cubic centimeter originally contained of hydrogen or of chlorine. Thus we have 2 cubic centimeters containing, of uncombined gases, twice as many particles as is contained in that volume after combination. Avogadro's hypothesis solved the difficulty. By premising two different orders of particles, now termed atoms and molecules, the solution was plain. According to him, each particle, or molecule, of hydrogen is a complex; it contains 2 atoms; the same is the case with chlorine. When these gases combine, or rather react, to form hydrogen chloride, the phenomenon is one of a change of partners; the molecule, the double atom, of hydrogen splits; the same is the case with the molecule of chlorine; and each liberated atom of hydrogen unites with one of chlorine, forming a compound, hydrogen chloride, which equally consists of a molecule, or double atom. Thus 2 cubic centimeters of hydrogen chloride consist of a definite number of molecules, equal in number to those contained in 1 cubic centimeter of hydrogen plus those contained in 1 cubic centimeter of chlorine. The case is precisely similar if other gaseous compounds be considered.

Berzelius was at first inclined to accept the theory, and indeed went so far as to change many of his atomic weights to make them fit it. But later he somewhat withdrew from his position, for it appeared to him hazardous to extend to liquids and solids a theory which could be held only of gases. Avogadro's suggestion accordingly rested in abeyance until 1858, when Cannizzaro, Professor of Chemistry in Rome, published an essay in which all the arguments in favour of the hypothesis were collected and stated in a masterly manner.

Although as early as 1811 a distinction had been drawn between the two classes of particles, atoms, or single particles of elements, and molecules, or congeries of atoms, which may either be of one kind, in which case the molecule is one of an element, or of different kinds, in which case the molecule is one of a compound, yet, as we have seen, the theory was not accepted by chemists and physicists until after 1858.

Inasmuch as physical chemistry rests on the molecular hypothesis of matter, researches before that date referred merely to the physical properties of matter, and just conclusions could not be drawn from them. It is necessary, in many very important researches, to pay attention to data considered with reference to equal numbers of molecules, instead of to equal masses of substance; and relations really simple remained undiscovered until the molecular hypothesis was generally adopted.

Yet many interesting observations were made before the middle of the eighteenth century, of great value in themselves, although their true bearing was not evident until the molecular hypothesis of matter had been established.

For example, Boyle's law (1662) relating to the compressibility of air was found to apply with more or less accuracy to the compressibility of other gases; and Gay-Lussac's or Dalton's law (1808) dealing with the expansion of gases with temperature, also holds approximately for all gases. The progress of science, however, has always been characterized by the discovery of approximate relations; the divergence from exactness has generally at first been attributed to the imperfection of the observations; and with improvements in apparatus, and with introduction of extreme conditions, these "laws" have always been discovered to be only approximately applicable; to render them more in accordance with fact, modifications have had to be introduced which lessen the deviations; but all that can be said of any so-called "laws" is that at the best they represent the results of measurement as accurately as the methods of experiment allow.

It is seldom the case that the causes of divergence can be fully discovered. Yet in some instances it is possible to surmise that the cause is known, even although the phenomena are too complicated to be solved numerically. The moon pursues an approximately elliptical course round the earth, due to her own proper motion and to the attraction of the earth; yet the path is influenced by the attraction of the sun, and in a lesser degree by that of the planets, and in a still smaller by that of the fixed stars. Owing to the number and complexity of these various attractions, it is impossible to do more than approximate numerically to the actual path of the moon's orbit; yet as many of these attractions are almost inconceivably minute, their effect may be disregarded. In such an instance the law of attraction is a simple one; but with molecules, instead of masses, the laws of attraction have still to be discovered.

Applying this conception to Boyle's and Gay-Lussac's laws, it was soon discovered that they held only with approximation; and in 1829 Dulong and Arago, and later Pouillet, Regnault, and Natterer, investigated the variation of the product of pressure and volume, which, according to Boyle's law, should remain constant so long as temperature is stationary. The investigation from a practical point of view was continued by Amagat, Mathias, Ramsay and Young, and others; and from

INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

To define exactly the provinces of the Sciences of Physics and Chemistry is not easy. The definition that the object of Chemistry is the study of the changes which matter undergoes during the formation and decomposition of compounds, while that of Physics has reference to changes which affect matter independently of its composition, hardly meets the case. It is true that it is possible to deduce certain laws relating to the properties of matter, which are valid irrespective of the chemical composition of the matter; but such laws deal with the behaviour of matter in motion, or acted on by gravitational or other forces which apply only to matter in bulk. For example, Newton's law of "gravitation"—that two masses approach each other as if impelled by a force which varies directly as their masses, and inversely as the square of the distance which separates them—takes no cognizance of the nature of the matter which attracts: the law is not affected by the chemical composition of the acting bodies. Similarly, the laws dealing with inertia are true, whatever the nature of the matter to which these laws apply. But when phenomena relating to change of volume by pressure, to the surface phenomena of liquids, to electricity, to heat, light, and other forms of wave-motion, are considered, the laws deduced from them contain specific

constants, so that their numerical application can be made only when these specific constants are known. Thus although the same differential equation governs the flow of heat in all kinds of matter, it contains a specific constant, viz. the "conductivity;" and as this varies for different kinds of matter, the chemical nature of the substance becomes a factor in the problem.

The birth of physical chemistry may be said to date from the recognition of this fundamental idea; where the laws or generalizations regarding properties of matter depend not merely on the masses or rates of motion of the objects considered, but also on their composition and chemical nature, their consideration falls under the heading "Physical Chemistry."

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Early researches of a physico-chemical nature were made in 1819 by Dulong, Director of the École Polytechnique at Paris, in conjunction with Petit, Professor of Physics there. These led to the discovery that equal amounts of heat are required to raise equally the temperature of solid and liquid elements, provided quantities are taken *proportional* to their atomic weights;

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be referred to atomic or molecular weights. Hence the determination of specific heats has been undertaken mainly by chemists; and the data obtained are among the earliest examples of physico-chemical constants.

The relations discovered by Gay-Lussac between the volumes of gases and their combining proportions stimulated others to investigate the question whether similar relations could not be found for liquids and solids. The first successful attempts were made by Hermann Kopp in 1842. The number of cubic centimeters of liquid at its boiling point, obtainable by condensing that volume of gas which contains the molecular weight of the liquid expressed in grams, was termed by Kopp the "specific volume." But it has since been found preferable to retain this term for the reciprocal of the density, *i.e.* for the volume occupied by one gram of the substance; and to substitute the term "molecular volume" for the constant suggested by Kopp. Working with carbon compounds, it was easy, by subtraction, to ascertain the difference in molecular volume for compounds differing by CH_2, *i.e.* the difference between consecutive compounds in a homologous series, and so to arrive at values for individual elements. It was then possible to calculate the molecular volumes of compounds by adding together the atomic volumes of the elements which they contained. The investigation was continued by Ramsay, Thorpe, Lossen, Schiff, and others; and it transpired that, as a rule, elements in compounds retain the atomic volumes which they possess in the free state; that the constitution of a compound has an appreciable influence on its molecular volume; and that certain elements are capable of assuming different volumes, according to the manner in which they are combined.

Properties which, like molecular weights and molecular volumes, can be numerically valued as the sum of the values of similar terms for elements, are on Ostwald's suggestion termed "additive." Those which are influenced by constitution, as to some extent molecular volumes, are termed "constitutive;" and those which, like gaseous pressures, depend wholly on the number, and not on the nature of the molecules, are termed "colligative." It was soon discovered that other properties of matter could be treated so as to exhibit their "additive" nature; among these are: the molecular refractive index, or the relative retardation which different compounds and elements offer to the passage of light (Gladstone and Dale, 1858; Landolt, 1864; L. Lorenz and H. Lorentz, 1880; Brühl, 1880); the dispersion of light, or the relative angle which passage through a prism separates rays of known wavelength (Gladstone and Dale, Kanonnikoff); the molecular rotation of the plane of polarized light by its passage through transparent chemical compounds in a magnetic field (Perkin); and molecular coefficients of viscosity (Thorpe and Rodger).

It is, however, also possible to treat such data partly from a "colligative," partly from a "constitutive" point of view; and attempts in this direction, more or less successful, have been made by Schröder and by I. Traube. The latter has been able to apply his method also to molecular volumes in solution in various solvents.

The surface energy of liquids has been shown by Eötvös (1886), and by Ramsay and Shields (1890), to have a simple relation to their molecular weights. At and above the critical point of a liquid it no longer possesses a surface, for liquid and gas are one. As the temperature falls below the critical point, however, the surface energy increases; and the rate of increase for equal numbers of molecules on a liquid surface, is approximately equal for all normal liquids. This affords a means of determining the molecular complexity of compounds and elements in the liquid state, for it is a colligative property. Other methods have yielded evidence corroborative of the quantitative results deduced from measurements of surface tension;

for example, the ratio between the density of a substance at its critical point and its normal gaseous density (Young), the rate of variation of its vapour pressure with increase of temperature, and similar properties.

The distinguishing characteristic of chemical compounds is their constant composition. But it is often difficult to decide whether or not a particular substance has or has not definite composition. Substances which do not exhibit constancy in this respect are termed "mixtures," and such mixtures sometimes consist of compounds mixed with excess of one or other constituent. The investigation of the nature of mixtures, accordingly, has long been regarded as the legitimate sphere of the chemist.

The first definite law regarding mixtures was discovered by Dr. Henry in 1803; it refers to solution of sparingly soluble gases in water. It is: *The amount of gas absorbed or dissolved by a given amount of liquid is proportional to the pressure of the gas.* As, however, the volume of the gas is inversely proportional to the pressure, it follows that a given quantity of liquid always dissolves the same volume of gas, whatever the pressure, temperature, of course, being maintained constant. A convenient way of stating the same fact is to use the word "concentration" to signify the quantity of substance in unit volume; it then follows that the concentration of the gas in the space occupied solely by gas is proportional to the concentration of the solution of the gas in the liquid, for by doubling the pressure the concentration of the gas is doubled, for twice the weight is contained in unit volume; and as the amount in solution is also doubled, its concentration is increased in the same proportion.

Henry's discovery was extended in 1807 by Dalton to the case of gaseous mixtures. His law is: *If a liquid is exposed to a mixture of gases, the amount of each gas dissolved is proportional to its partial pressure, and to its solubility.*

The solubility of gases in liquids generally decreases on at *during any chemical process is the same whether the process* s *place in one or in several stages.* Actual determinations of heat evolved during combustion of various substances, and the heat-changes which take place on solution, were made by rews (1841 and subsequent years) and by Graham (1843); Favre and Silbermann greatly added to our knowledge of of this nature (1852–1853). The most remarkable series searches on the heat-changes which accompany chemical n are due to Julius Thomsen of Copenhagen, and to Mar- Berthelot of Paris; the former published his first treatise 53, and the latter in 1865, and they have continued their igations almost to the present day (1903).

ch of these authors enounced a principle, which has quently turned out to be incorrect, viz. that those chemical ons take place which are accompanied by an evolution of . But this incorrect hypothesis led to the production enormous mass of experimental work. The evolution of ring the formation of numerous compounds from their ts, the heat-changes occurring during the conversion of mpound into another, the heats of combustion of com- of carbon and other elements, that evolved during the zation of bases by acids and during the progress of ic and isomeric change, have, in many cases, been red, and many interesting conclusions have been arrived One of the most interesting is the fact that on neutralizing ilute solution of a monobasic acid by a monoacid base, rly the same amount of heat is evolved in most cases; and tracing of this fact to its cause—that such an action is ompanied by only one chemical change, the combination of hydroxyl ion, OH', of the base with the hydrogen ion, $H^{\cdot}$, the acid. The metallic and acid ions remain, for the most t, unaffected by mixing their solutions. When combination urs, or where the acid or the base, in solution, exists not olly in the state of ions, the regularity no longer holds.

Other interesting results have been arrived at in the case explosive bodies, which are always endothermic, *i.e.* are form with absorption of heat; while stable bodies are generally p duced with heat evolution. With rise of temperature, su stances formed with evolution of heat become more unstabl and the converse is also true, that endothermic substanc become more stable on rise of temperature.

On the whole, however, little of theoretical importance h been deduced from the very numerous data of therm chemistry. It is true that F. W. Clarke has recently publishe the outlines of an attractive theory, which makes it possibl to calculate the heats of formation of many compounds from simple considerations; but the accuracy of Clarke's deductio has been disputed by Julius Thomsen.

The first application of electricity to chemistry dates from the time of Priestley (1772); he proved that the effect of passing electric sparks through air was to produce an acid substance, which he supposed to be carbonic acid; but in 1775 Cavendish carried out a marvellously careful set of experiments, and showed that the acids actually produced were nitrous and nitric. Not long afterwards van Marum (1785) and van Trostwyk and Deimann (1789) showed that hydrogen and oxygen result from the action of powerful sparks on water.

Shortly after (1791) Galvani discovered that a feeble current of electricity caused the muscles of a frog's leg to contract, and Volta invented his "pile." With such a "pile," Nicholson and Carlisle "decomposed water" (1800), and found that from the wire attached to the zinc disc oxygen was evolved, while from the other wire bubbles of hydrogen escaped. At the same time the water round the former became acid, and round the latter alkaline. That acid and alkali could be produced by the decomposition of "pure" water was a puzzle to many; and it was not until Humphry Davy showed in 1800 that alinity and acidity were due to the electrolysis of minute of salt, dissolved out of the vessel in which the water was ied, and that pure water in vessels of gold or platinum practical non-conductor, and gave rise by its decomn to no alkali or acid, that the anomaly was explained.

vy also evolved a theory by means of which he enıred to connect electrical with chemical phenomena. g from the known fact that acids or bases in contact netals acquire an electrical charge, he argued that the nust be the case with atoms; that in entering into chemical nation they acquire electrical charges of different sign, ohere, owing to the same reason which causes electrical ion of oppositely electrified bodies. According as the is greater or less, the chemical attraction is powerful or . Davy found the difference of chemical potential to se with rise of temperature, and drew the not unnatural ision that this increase runs parallel to the increase of cal affinity, which causes combination more readily at a han at a low temperature. Indeed, Davy did not regard as two different phenomena, one the cause, the other the , but he regarded them as essentially the same.

ecomposition by an electric current he believed to be a al of the phenomena of combination. In giving the of the decomposing compound opposite charges to those they had acquired by their combination, the atoms were ed to their previously neutral state; the positive atoms or s were attracted to the negative pole; their positive charges neutralized by a corresponding negative charge from the and the atom or group was liberated in the free state.

avy's views made no lasting impression, for they were ly afterwards superseded by those of Jacob Berzelius 6). Berzelius held the view that all chemical compounds isted of a combination of two opposite constituents. To view he was led by the observation that an electric current

apparently decomposed salts into an acid portion and a b
portion, each of which goes respectively to the negative or
the positive pole; combustible substances, alkalies or alkal
earths, collect at the positive pole, while oxygen, acids, and
general oxidized substances go to the negative pole. He
believed that the decomposition of mixtures or of compou
was in compound proportion to their chemical affinity an
their surface of contact, and that the absolute amount
decomposition was proportional to the quantity of elec
and that this varied with the surface of contact betw
metal and the conducting liquid; it was also supposed b
to be proportional to the conductivity of the solution.
course of the reactions occurring during decompositi
believed to be influenced by the affinity of the comp
for the material of the wires, by the mutual affinity
constituents, and by the cohesion of the resulting comp
To justify these suppositions he made the hypothesis th
atom contains electric charges of different amounts;
general both a positive and a negative electric charge,
each pole. His theory differed from that of Davy ess
in this, that while Davy believed that the atoms acquired
charges only by contact with each other, Berzelius imagi
atoms to be endowed from the start with electrical ch
But although any atom contained both a positive and neg
charge, they were not necessarily equal in amount; hence so
atoms were essentially negative, whilst others were essential
positive. During combination, the oppositely electrified ato
attracted each other, and by equalizing their charges, more
less, heat and light were the accompaniments of the partial
complete restoration of the electrical neutrality. Berzeli
himself acknowledged, however, that the neutralization of t
electric charges removed the cause of the persistence of t
compound, if chemical affinity were considered to be due
electric attraction. But Berzelius made use of his "binar

theory more as a means of classification than for the purpose of explaining chemical or electrical phenomena; and owing to that advantage it persisted for long.

The next advance in the subject was due to Michael Faraday (1831–1838). His first statement was: *The amount of a substance decomposed by an electric current is proportional to the amount of electricity which passes through it.* This was soon after followed by the important law which goes by his name: *If the same current passes through several electrolytes, the amounts of the different substances separated from the compound are proportional to the chemical equivalents of the substances separated.* The same amount of electricity, he showed, always liberated the same amount of explosive mixture of oxygen and hydrogen from dilute sulphuric or hydrochloric acid, whatever the "strength" of the current, the size of the electrodes, the dilution of the liquid, or the temperature.

It was Faraday who introduced the term *electrolysis* to signify the process of separation of the constituents of a compound body by means of an electric current; the conductor, of which the components undergo such separation, he called the *electrolyte;* the moving parts were termed by him *ions* (or "movers"), and those which go towards the *anode* he called the *anions*, and similarly, the ions which move towards the *kathode* were termed by him the *kations* (*ana* = up; *kata* = down; *hodos* = a way).

Faraday was careful to point out that the passage of a current through an electrolyte, and the separation of the ions at the electrodes, although they are concurrent, are yet absolutely distinct phenomena.

While Davy's view that the products of electrolysis are the metal or hydrogen, on the one hand, and the non-metal, or electro-negative group, on the other, had been overshadowed by Berzelius's contention, that one product is an acid, and the other a base, the question was not settled until Daniell, Professor at King's College, London (1839), showed that if a current be passed through "water" (dilute acid) as well as through a solution of sodium sulphate, the same amount of hydrogen is collected in each case; but in the latter, an equivalent of "soda" (sodium hydroxide) is also set free. Hence the current would appear to be doing double work in the solution of sodium sulphate; not merely liberating the correct amount of hydrogen, but also liberating the soda. He pointed out the obvious explanation: that the primary product of the electrolysis of the sodium sulphate is sodium, and that the hydrogen is really produced by the action of that metal on the water, at the moment of its liberation.

Early in the days of electro-chemistry (1805) a hypothesis was brought forward by Grothuss to explain a phenomenon which had been pointed out by Davy, namely, that the element liberated at one pole has not been driven bodily from the opposite pole to the one at which it is liberated. As a striking proof of this, he caused the current by which "water" was electrolysed to pass through his own body; and it was inconceivable that the same atom of oxygen, for example, could have passed from the negative to the positive pole through his organism. Grothuss imagined the atoms to be already charged. The atoms of oxygen and hydrogen in the water molecules gave up their charges to their respective poles, and escaped; the neighbouring atoms changed partners, those at the end of the chain combining with the atoms left without partners. But Clausius (1857) disproved Grothuss's theory, which had maintained its ground for over half a century. He pointed out that if a certain "force" is required to effect decomposition, no decomposition should take place until that force has come into operation; as a matter of fact, however, the smallest conceivable electric "force" is sufficient to effect decomposition of an electrolyte. He therefore imagined that in any electrolytic solution some of the atoms are continually changing partners ıat they move under the influence of the current at the t when they are unattached, that is, while the exchange ing place. This hypothesis had previously been put d by Williamson, with the view of explaining all chemical ; some molecules, he supposed, were always undergoing ıposition; their constituent atoms, or groups, however, ıt necessarily reunite, but were ready to unite with those er molecules which also had undergone decomposition.

ıe relative rate of motion of the ions was first measured ttorf. Although it had been noticed by Faraday (1834), Daniell and Miller (1845), that during the electrolysis ılt the salt became more concentrated in the neighbour- ɔf one pole, and more dilute round the other, it was not 853 that the true explanation was found by Hittorf in t that the two ions do not move at an equal rate. If o, there is no such alteration of concentration. But in ıre numerous cases, where their rate of motion is different, t concentrates round the pole to which the more rapidly g ion is travelling.

ttorf also pointed out that compounds, solutions of which od conductors of electricity, are precisely those bodies are most susceptible of chemical reaction. In later his dictum has proved one of great importance.

curate measurements of the rate of passage of charged ırough their solutions were first made by Kohlrausch 9, with this remarkable result: that the ions move ndently of one another. Hence the electrical conduc- f any salt may be arrived at by the *sum* of the rates of rt of its ions.

rther progress was made in 1887 by Arrhenius, who l that, on sufficient dilution, all salts arrive at a maximum tivity, of the same order of magnitude; and he deduced his that, with increasing dilution, a larger and larger r of molecules become ionised, *i.e.* resolved into ions.

Indeed, many salts, in fairly concentrated solution, are already largely split into ions; while acids, on the other hand, even very small concentration, are to some extent in the non-ionised form. The reactivity of a salt, he contended, was due to the actual number of ions present in unit volume. And van't Hoff showed the proportionality between the relative number of ions, thus determined electrically, and the osmotic pressure which they exert, as well as their influence in raising the boiling point and depressing the vapour pressure or the freezing point of the solutions which contain them.

The connection between the amount of energy expended electrically in the cell of a battery, and the heat evolved when the reaction between the constituents of the cell proceeds without production of a current, or with a closed circuit, was first calculated and experimentally proved by Joule and Thomson (Lord Kelvin), the latter of whom summed up the results of the investigation in the proposition: *The intensity of an electro-chemical apparatus is, in absolute measure, equal to the mechanical equivalent of as much of the chemical action as occurs by means of a current of unit strength, in unit time.* But experiments by Boscha, Raoult, and others did not always succeed in corroborating the truth of this assertion. The anomaly was explained by Helmholtz, as well as by Willard Gibbs (1878) in his great work. The discrepancy was caused by the neglect to take into account the temperature-coefficient of the electromotive power of the particular cell employed. If this is small as, for example, in a Daniell's cell, in which zinc is replaced by copper, the agreement with Joule and Thomson's stateme is a close one; but if it is large, as in many other instanc the necessary correction must be introduced in order th experiment and theory give the same result. The furth development of electro-chemistry belongs to the present da and will be thoroughly considered in the volume devoted that subject.

The connection of chemical action with light is a subject which has attracted much attention, owing to its connection with the practical aspect of photography on the one hand, and with astronomy on the other, in the form of spectroscopy. But even yet few general conclusions have been drawn.

The fact that silver-salts are alterable by light was observed as early as 1727 by Schultze; and Scheele, the discoverer of oxygen, observed that this action is due chiefly to the violet part of the spectrum (1777). Senebier made quantitative experiments in 1784; and Daubeny, in 1836, made similar quantitative experiments on the influence of different colours of the spectrum on the absorption of carbon by plants.

It was for long believed that three distinct varieties of waves were emitted by luminous bodies; waves of light, of heat, and of chemical action; but it appears that all waves may have all three effects, and that the wave-length of those waves which produce the maximum of chemical action depends on the kind of chemical action which results from them. Thus, while the maximum effect on plant-life is produced by light of such a wave-length that it has also nearly the greatest luminosity, the maximum effect in decomposing silver bromide is caused by vibrations in the ultra-violet part of the spectrum; and heat effects are produced by vibrations in the infra-red.

It has been pointed out by Mayer that while, generally speaking, the effect of ether waves in promoting chemical action is merely that of causing it to start, so that energy is lost, the action on living plants is of an opposite character, for by its influence energy is stored. The action in the first case is one resembling catalysis, and merely increases the rate at which chemical action proceeds; while in the second, the radiant energy from the sun is stored by means of the plant as chemical energy.

Many attempts, more or less successful, have been made to measure, by the chemical changes produced, the intensity of the radiations which produce these changes; the best kno are the researches of Bunsen and Roscoe (1851–1862), Draper (1857). Many more recent researches have, howe been made.

The development of spectroscopy has of recent years be very rapid, so far as relates to the measurement of the spec of different substances. Although the refraction of light first explained by Newton, and investigated in the early half the eighteenth century by Brewster, rapid progress was ma when Kirchhoff discovered, in 1860, that all substances e rays of light of the same wave-length as those which th absorb. The introduction of the spectroscope as a mea of analysis by Bunsen and Kirchhoff drew attention to t advantage of the study of spectroscopy, and established ma important laws. The fact that gases made luminous by electric current of high potential could be made to e different kinds of spectra, according to the nature of th discharge, was the discovery of Plücker and Hittorf (1865) and the fact that each compound, if it can only stand the te perature at which it emits luminous rays, has its own speci spectrum was first announced by Mitscherlich in 1869.

The first theoretical discussion of spectra is due to Maxw (1875); he pointed out that harmonic relations should found between the wave-length of the lines of the spectra any substance. Mascart, Stoney (1871), and Lecoq de Bo baudran (1889) have shown that such "harmonic relation exist in some cases; and other authors have sought to establi such relations; the most successful is due to Balmer, who formula has yielded excellent results in the hands of Rydbe Runge and Paschen, Kayser, Lorenz, Zeeman, and others.

There is, however, a vast unexplored field in spectroscop for although the visible waves, as well as those in the ultr violet part of the spectrum, have been investigated in ma instances, the infra-red waves have been hardly looked fo

Langley, indeed, has measured the lines in the infra-red part of the solar-spectrum by means of his "bolometer," an instrument capable of detecting very minute differences of temperature; but this instrument has been little applied to the spectra emitted by gases or by hot solids.

Speculations regarding the reason of chemical combination date from the earliest times. The word "affinity," or "chemical affinity," calls us back to the time of Hippocrates, whose view was that "like draws to like;" that substances which combine must have something in common, like wine and water, silver and gold. As solution and mixture passed in those days for combination, there was some reason for his dictum. Empedocles, the first atomist, held a different view, founded on imaginary hates and loves between the atoms. In the Middle Ages, even quainter ideas are to be met with; that the particles of the acid solvents are sharp, like needles or spears, and that they transfix and support the particles of dissolved metal; that sweet liquids are sweet, because of the rounded form of their ultimate particles; and that they therefore have not a similar solvent action. With Newton a new view arose. He himself did not believe that affinity was due to an attraction identical with that of gravitation; but leant to the view that the force varied inversely with some higher power of the distance than the square. But Buffon, the French naturalist, in spite of Newton's well-considered thought, supposed that the form of the objects attracting—the ultimate particles—could make it possible that the laws of the inverse square held for chemical attraction; and his views were widely disseminated and accepted.

Davy's and Berzelius's electro-chemical theories have already been alluded to, and need not be further discussed here.

Attempts to arrange qualitatively the order of affinity of the elements for each other were frequently made in the eighteenth century. As early as 1718, Geoffroy arranged in order variou chemical substances (for elements in the modern sense of th word were even then not recognized) in the order of what h supposed to be their affinity for each other. For instance, under "metallic substances" we find the order—iron, copper, lead, mercury, silver, as regards their affinity for nitric acid; and for vitriolic acid the order was—sulphurous or oily principle, fixed alkali, volatile alkali, absorbent earth (*i.e.* calcium carbonate), iron, copper, silver, and so on. The idea which guided him he expressed thus: "Whenever two substances, which have some inclination to combine, are combined with each other, and a third is presented to them which has more affinity to one of the two than the other, that other is expelled." The same idea was fully elaborated by Torbjorn Bergmann in 1783. He distinguished between various kinds of attraction: for example, particles of the same kind were held together by *attractio aggregationis*; compounds remained compounds by virtue of *attractio compositionis*, which might be of two kinds, according as they had been prepared in solution (*attractio solutionis*) or by fusion (*attractio fusionis*). Simple expulsion of one constituent out of a compound by the action of another was due to *attractio simplex electiva*; while exchange between the constituents of two compounds was caused by *attractio duplex*. Attempts not merely to determine the order, but also the relative amount of such affinities, were made by De Morveau (1793); he attempted to ascertain the relative affinities of metals for mercury by measuring the weights required to separate plates of a number of metals of the same size from a surface of mercury, and concluded that as adhesion and affinity must be fundamentally the same, he was measuring relative affinity. He also gave six laws of affinity: that only liquids act; that affinity takes place only between the smallest particles of substance; that the affinity between any two substances is partly conditioned by the relative amount of each; that chemical affinity acts only it can overcome cohesion; that compounds differ entirely in operties from their constituents; and that affinity is greatly fluenced by temperature.

We have here a statement that the relative amounts of bstance present influence their behaviour as regards a third. his law was originally stated by Wenzel in 1777, in this orm: The affinities of bodies for a common solvent are nversely as their rates of solution in that solvent; also, that he strength of chemical action is proportional to the concentration of the acting material. Count Berthollet, independently of Wenzel, enunciated the same doctrine in 1799, and stated clearly that it was impossible, as Bergmann had attempted, to arrange substances in a definite order of chemical affinity, but that the affinity was deeply affected by the relative amounts of substances present. He succeeded in reversing the actions which had hitherto been supposed to decide the order of chemical affinity: for example, he decomposed barium sulphate by boiling potash; potassium sulphate by boiling milk of lime; calcium oxalate by nitric acid, and so on. Although in each case only a partial decomposition was attained, yet that decomposition occurred at all was regarded by him as a proof that a large quantity of a reagent could reverse the order of chemical affinity. He regarded these reversed actions to be due to the small surface of the precipitate, compared with the large and constantly renewed surface of the acting liquid; so that when a liquid acts on a solid, the activity of the liquid is conditioned not by its total amount, but by the degree of its concentration; and similarly for gases. For when a gas is liberated by any reaction, it removes itself, and can no longer act on the dissolved substances; hence a comparatively small quantity of reagent is capable of liberating a large quantity of gas. The elasticity of the gas may be regarded as a force acting in opposition to the affinities of liquids. Combination may be either helped or hindered by a rise of temperature; helped, if the rise of temperature so diminishes the cohesion of the acti substances as to increase chemical action; hindered, if o of the substances changes its state by the rise of temperat and removes itself from the sphere of action. The action o solvents is in reality the overcoming of cohesion, so that th affinities of the dissolved substances can manifest themselves.

It is thus evident that Berthollet's ideas on the measureme of chemical affinity differed in important respects from tho of his predecessors. According to him, at least one of th reacting substances must separate, in order that a reaction sh take place; the state of equilibrium is thus destroyed, and th reaction proceeds until so much of one or other substanc separates as to restore the balance.

But Berthollet was misled into making the false statement that the composition of compounds may vary within limits, and that the proportion of the constituents of each compound depends on the relative proportion in which the constituents are present during the process of its formation. Proust, a countryman of Berthollet's, refuted Berthollet's statement by direct experiment, and showed that the supposed compounds on which Berthollet based his contention were not really definite compounds, but mixtures. The definite and invariable composition of chemical compounds, as has been already stated, was fixed by Dalton and by Berzelius.

While, then, it is true that the relative amount of a compound formed during any reaction is conditioned by the proportions of the reacting substances present, it does not follow that the composition of the compound itself is thus affected; nor is it true, as Berthollet fancied, that the relative affinities of acids are to be gauged by the relative amounts required to saturate a given base. While Gay-Lussac saw this error, he defended Berthollet's main contention, and maintained that the partition of acids with a base sufficient to saturate only one of them was affected by the relative amounts of the acids esent. But the difference between altering the relative amount a compound formed and altering the composition of the ompound is a fundamental one.

Berthollet's work, *Essai de Statique Chimique*, was conseuently soon forgotten; and it was not until 1835 that the uestion was revived by Persoz, Professor at Strassburg, who ttempted to give a table analogous to Bergmann's of the relative ffinity of oxides for acids. And Berthollet's views were resuscitated for analytical purposes by Rose in 1842, and later, in 1853, by Bunsen. Bunsen exploded a mixture of hydrogen and carbon monoxide with an amount of oxygen insufficient for both, and concluded that instead of a gradual progression in the proportions of water vapour and carbon dioxide produced, the ratio remained definite until a certain excess of oxygen was present, and that it then altered suddenly; so that there was always a definite molecular proportion between the amounts of the two products of oxidation. Similar results were obtained by his assistant Debus, in precipitating carbonates of calcium and barium by the action of carbon dioxide or their hydroxides. But these experiments were subsequently proved to be erroneous.

The law of "mass-action," although foreshadowed by researches of Biot (1835) was first stated in precise terms by Wilhelmy in 1850. In order to examine the state of equilibrium in any system, it is clear that the conditions must not be changed: for example, the solution must not be concentrated by evaporation; nor must other substances be added; nor must the temperature be altered; nor must the solvent be changed, as, for example, by the addition of alcohol to an aqueous solution; hence some physical property must be made use of, which shall reveal the result of the change which has taken place, without disturbing equilibrium.

For this purpose Wilhelmy made use of the rotation of the plane of polarized light caused by cane-sugar, and by its products of decomposition on treatment with an acid, dextrose and levulose. In this way the rate of change could be measured without the introduction of any foreign substance. This law and its consequences will be fully considered in the volume on chemical dynamics. In 1855, J. H. Gladstone made use of the colours of solutions of reacting substances and their products to investigate the position of equilibrium, and in one instance he employed the rotation of polarized light; and to him belongs the credit of pointing out that after this manner tables of relative affinity could be constructed. Berthelot and Péan de St. Gilles, in 1862 and 1863, in investigating the action of acids on alcohols, which is attended with the formation of esters, did much to elucidate the nature of chemical action. They showed that the action is a gradual one; that it is never complete, but that the amount of ester formed tends towards a limiting value; and that this limit is the same, whether it be reached by the action of acid on alcohol, or of water on ester. They also showed that the rate of action, but not the limit, was greatly increased by rise of temperature, and that pressure has little influence on the process. Their conclusion agreed with that of Wilhelmy, that the quantity of ester formed at any moment is proportional to the product of the acting masses, and inversely proportional to the volume they occupy.

About this date (1857) Deville began to publish his results of experiments on dissociation, which have already been alluded to. He drew an analogy between the temperature of dissociation of a compound and the boiling point of a liquid; or, to be more precise, the pressure exercised by a gaseous constituent of the dissociating body at a given temperature, and the pressure exerted by the vapour of a liquid at a given temperature. With rise of temperature, vapour pressure increases; and similarly with rise of temperature the pressure due to dissociation increases. Curiously enough, however, Deville was against the theory of mass-action; and yet his xperiments furnish one of the most striking proofs of the ustice of that doctrine.

The first attempt to determine the value of chemical affinity by help of the then recently developed ideas of thermodynamics is due to Julius Thomsen, of Copenhagen (1854). Defining "affinity" as that force which holds together the constituents of a compound, he believed that it was possible to measure the amount of that *force* by measuring the *heat* evolved in a reaction by which the body was formed, which would be equivalent to the heat required to decompose the body—that is, he thought it possible to measure a *force* in terms of an *energy*. He also believed that all chemical changes which take place spontaneously, or after being started, are necessarily accompanied by an evolution of heat. It is true that he was acquainted with changes, such as the solution of salts in water, which were attended by absorption, and not evolution of heat; but he attempted to explain away such cases by premising that it was only purely chemical actions which were attended by evolution of heat.

In 1867, Berthelot independently announced the same principle; and a somewhat heated discussion between Thomsen and Berthelot took place in 1873, as to claims of priority and as to the exact nature of the statement involved, which need not be further pursued, inasmuch as the matter in dispute was a false statement.

But the question had been solved by Waage, former Professor of Chemistry, and Guldberg, Professor of Mathematics, at Christiania, who published, in 1865, a pamphlet termed *Études sur les Affinités chimiques.* The fundamental idea of this work was the law of mass-action: that *the chemical action is proportional to the quantities of substances acting; the last being determined by the amounts in unit volume.* If two substances act on each other, the action is proportional to the relative amount of each, and will be zero if the amounts of acting bodies is zero, and therefore it is proportional to the product of the two. Further, the action will depend on the nature of the substances, on the temperature, and on other circumstances; these influences can be expressed by a factor, hence the "force" of the chemical affinity can be represented by the expression kpq, if k is the factor, and p and q are the acting masses. But this action is balanced by forces acting in opposition to the formation of the new system, which tend to restore the primary condition of the substances. If the substances formed by the original reaction are p' and q', and the new factor k', equilibrium will be established when $kpq = k'p'q'$. Although it is not possible to calculate the actual amount of the "chemical forces," it is possible to calculate their ratio, by knowing the position of equilibrium, when the reaction has gone as far as it will, under a given set of conditions. The actual result of such calculations is, however, to give the relative velocities of chemical reactions; and van't Hoff, in 1877, pointed out that it is sufficient to confine attention to such velocities, and not to ascribe the velocities to an impelling force, and thereby to introduce mechanical ideas which are unnecessary for the purpose. Guldberg and Waage proved their thesis by many experimental researches; while in 1869 Julius Thomsen had shown that the problem can be solved by thermochemical measurements. Ostwald, in 1876, made quantitative measurements of volume-changes during reactions, which also afforded data for the proof of the law.

Horstmann was the first to apply thermodynamics to chemical processes (1869), treating first the problems of dissociation. The similarity between dissociation and vapour pressure makes it possible to treat the former in the same manner as the latter, because both classes of reaction are reversible. Berthelot's and Thomsen's law, implying that that change necessarily takes place which is accompanied by a dissipation of *energy*, was replaced by another: *that of all possible* *systems that one is most stable in which the entropy is at its maximum.* The consideration of this doctrine will be found in the volume on Thermodynamics. This principle was later announced by Lord Rayleigh. The most remarkable advance in this direction, however, is due to Willard Gibbs (1874–1878). It is hardly too much to say that all subsequent advances are merely applications and variations of Gibbs's fundamental considerations. In his epoch-making work, Gibbs treats of the chemical potential of a substance, of coexisting phases of matter, of cases of mixture of ideal gases as regards their equilibrium with liquids and solvents, or with solids, of surface-tension, and of electric action between bodies.

In van't Hoff's *Études de dynamique chimique* (1884), numerous instances are adduced of the application of the laws of chemical dynamics, and the influence of temperature was especially studied. And after Arrhenius of Stockholm had brought out his theory of the independent existence of ions in solutions (1884), van't Hoff in 1887, as has already been narrated, drew deductions from measurements of osmotic pressure by de Vries and by Pfeffer, of the depression of vapour pressure and of rise of boiling point of solvents caused by dissolved substance, and of lowering of freezing points investigated by Raoult, and of Arrhenius's determinations of electric conductivity, and welded all these ideas into a homogeneous whole.

The present volume, which forms the first of the series of works dealing with physical chemistry which it is proposed to publish, treats of the Phase Rule, one of the subjects treated of by Willard Gibbs, in which many of the considerations touched on in the foregoing pages are introduced.

It is proposed, in subsequent volumes, to treat of *Stoichiometry*, or the various methods employed to determine atomic and molecular weights, and the classification of compounds (Professor Sydney Young, D.Sc., F.R.S.); of the Relations between Chemical Constitution and Physical Properties (Samue Smiles, D.Sc.); Electro-chemistry (R. A. Lehfeldt, D.Sc.); o Spectroscopy (E. C. C. Baly, F.I.C.); of Thermodynamic (F. G. Donnan, M.A., Ph.D.); and of Chemical Dynamic (J. W. Mellor, D.Sc.). In these volumes the main divisions of the subject will be covered, while each will be as complete a treatise in itself as is possible, without undue overlapping. In each the subject will be brought up to the date of the latest discovery; and although it is, of course, impossible to avoid compilation, original papers will be the chief sources of information; while each of the authors has special knowledge of the branch of which his work treats. It is hoped that these volumes will be published at short intervals; and if there is found to be a sufficient demand for them, it will be possible t issue frequent new editions, so as to keep abreast of a va subject, which is progressing at a rate hitherto unknown in th history of Chemistry.

THE PHASE RULE

CHAPTER I

INTRODUCTION

ieral.—Before proceeding to the more systematic treat- nt of the Phase Rule, it may, perhaps, be not amiss to give t a brief forecast of the nature of the subject we are about study, in order that we may gain some idea of what the ise Rule is, of the kind of problem which it enables us to re, and of the scope of its application.

It has long been known that if water is placed in a closed, austed space, vapour is given off and a certain pressure is ited in the enclosing vessel. Thus, when water is placed the Torricellian vacuum of the barometer, the mercury is ressed, and the amount of depression increases as the tem- ature is raised. But, although the pressure of the vapour reases as the temperature rises, its value at any given tem- ature is constant, no matter whether the amount of water sent or the volume of the vapour is great or small; if the ssure on the vapour is altered while the temperature is ntained constant, either the water or the vapour will ulti- ely disappear; the former by evaporation, the latter by densation. At any given temperature within certain limits, efore, water and vapour can exist permanently in contact one another—or, as it is said, be in equilibrium with one ther—only when the pressure has a certain definite value. same law of constancy of vapour pressure at a given temperature, quite irrespective of the volumes of liq vapour,[1] holds good also in the case of alcohol, ether, b and other pure liquids. It is, therefore, not unnatural the question, Does it hold good for all liquids? Is for example, in the case of solutions?

We can find the answer to these questions by stud behaviour of a solution—say, a solution of common water—when placed in the Torricellian vacuum. In t also, it is observed that the pressure of the vapour i as the temperature is raised, but the pressure is n independent of the volume; as the volume incre pressure slowly diminishes. If, however, solid salt is in contact with the solution, then the pressure again constant at constant temperature, even when the volun vapour is altered. As we see, therefore, solutions behave in the same way as pure liquids.

Moreover, on lowering the temperature of water, reached at which ice begins to separate out; and if now added to the system or withdrawn from it, n will take place in the temperature or vapour pressu latter until either the ice or the water has disappeare water, and vapour, therefore, can be in equilibrium another only at one definite temperature and one pressure.

In the case of a solution of common salt, howeve have ice in contact with the solution at different tem and pressures. Further, it is possible to have a in equilibrium not only with anhydrous salt (NaCl) with the hydrated salt (NaCl, $2H_2O$), as well as wit the question, therefore, arises: Is it possible to s general manner the conditions under which such systems can exist in equilibrium; or to obtain son ıto the relations which exist between pure liquids and soluons? As we shall learn, the Phase Rule enables us to give n answer to this question.

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[1] Except when the volume of the liquid becomes exceedi in which case the surface tension exerts an influence on pressure.

[2] For reasons which will appear later (Chap. IV.), the vc vapour is supposed to be large in comparison with that of tl liquid.

The preceding examples belong to the class of so-called "physical" equilibria, or equilibria depending on changes in he physical state. More than a hundred years ago, however, it was shown by Wenzel and Berthollet that "chemical" equilibria can also exist; that chemical reactions do not always take place completely in one direction as indicated by the usual chemical equation, but that before the reacting substances are all used up the reaction ceases, and there is a condition of equilibrium between the reacting substances and the products of reaction. As an example of this, there may be taken the process of lime-burning, which depends on the fact that when calcium carbonate is heated, carbon dioxide is given off and quicklime is produced. If the carbonate is heated in a closed vessel it will be found, however, not to undergo entire decomposition. When the pressure of the carbon dioxide reaches a certain value (which is found to depend on the temperature), decomposition ceases, and calcium carbonate exists side by side with calcium oxide and carbon dioxide. Moreover, at any given temperature the pressure is constant and independent of the amount of carbonate or oxide present, or of the volume of the gas; *nor does the addition of either of the products of dissociation, carbon dioxide or calcium oxide, cause any change in the equilibrium.* Here, then, we see that, although there are three different substances present, and although the equilibrium is no longer due to physical, but to chemical change, it nevertheless obeys the same law as the vapour pressure of a pure volatile liquid, such as water.

It might be supposed, now, that this behaviour would be shown by other dissociating substances, *e.g.* ammonium chloride. When this substance is heated it dissociates into ammonia and hydrogen chloride, and at any given temperature the pressure of these gases is constant,[1] and is independent of the amounts of solid and gas present. So far, therefore, ammonium chloride behaves like calcium carbonate. If, however, one of the products of dissociation be added to the system, it is found that the pressure is no longer constant at a given temperature, but varies with the amount of gas, ammonia or hydrogen chloride, which is added. In the case of certain dissociating substances, therefore, addition of one of the products of dissociation alters the equilibrium, while in other cases it does not. With the help of the Phase Rule, however, a general interpretation of this difference of behaviour can be given—an interpretation which can be applied not only to the two cases cited, but to all cases of dissociation.

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[1] Ramsay and Young, *Phil. Trans.*, 1886, **177**. 87.

Again, it is well known that sulphur exists in two different crystalline forms, octahedral and prismatic, each of which melts at a different temperature. The problem here is, therefore, more complicated than in the case of ice, for there is now a possibility not only of one solid form, but of two different forms of the same substance existing in contact with liquid. What are the conditions under which these two forms can exist in contact with liquid, either singly or together, and under what conditions can the two solid forms exist together without the presence of liquid sulphur? To these questions an answer can also be given with the help of the Phase Rule.

These cases are, however, comparatively simple; but when we come, for instance, to study the conditions under which solutions are formed, and especially when we inquire into the solubility relations of salts capable of forming, perhaps, a series of crystalline hydrates; and when we seek to determine the conditions under which these different forms can exist in contact with the solution, the problem becomes more complicated, and the necessity of some general guide to the elucidation of the behaviour of these different systems becomes more urgent.

It is, now, to the study of such physical and chemical equilibria as those above-mentioned that the Phase Rule finds application; to the study, also, of the conditions regulating, for example, the formation of alloys from mixtures of the fused metals, or of the various salts of the Stassfurt deposits; the behaviour of iron and carbon in the formation of steel and the separation of different minerals from a fused rock-mass. Wit ie help of the Phase Rule we can group together into classes ie large number of different isolated cases of systems in quilibrium; with its aid we are able to state, in a general ianner at least, the conditions under which a system can be n equilibrium, and by its means we can gain some insight into he relations existing between different kinds of systems.

Homogeneous and Heterogeneous Equilibrium.—Before assing to the consideration of this generalization, it will be vell to first make mention of certain restrictions which must oe placed on its treatment, and also of the limitations to which it is subject. If a system is uniform throughout its whole extent, and possesses in every part identical physical properties and chemical composition, it is called *homogeneous*. Such is, for example, a solution of sodium chloride in water. An equilibrium occurring in such a homogeneous system (such as the equilibrium occurring in the formation of an ester in alcoholic solution) is called *homogeneous equilibrium*. If, however, the system consists of parts which have different physical properties, perhaps also different chemical properties, and which are marked off and separated from one another by bounding surfaces, the system is said to be *heterogeneous*. Such a system is formed by ice, water, and vapour, in which the three portions, each in itself homogeneous, can be mechanically separated from one another. When equilibrium exists between different, physically distinct parts, it is known as *heterogeneous equilibrium*. It is, now, with heterogeneous equilibria, with the conditions under which a heterogeneous system can exist, that we shall deal here.

Further, we shall not take into account changes of equilibrium due to the action of electrical, magnetic, or capillary forces, or of gravity; but shall discuss only those which are due to changes of pressure, temperature, and volume (or concentration).

Real and Apparent Equilibrium.—In discussing equilibria, also, a distinction must be drawn between real and apparent equilibria. In the former case there is a state of rest which undergoes continuous change with change of the conditions (*e.g.* change of temperature or of pressure), and for which the chief criterion is that *the same condition of equilibrium is reached from whichever side it is approached.* Thus in the case of a solution, if the temperature is maintained constant, the same concentration will be obtained, no matter whether we start with an unsaturated solution to which we add more solid, or with a supersaturated solution from which we allow solid to crystallize out; or, in the case of water in contact with vapour, the same vapour pressure will be obtained, no matter whether we heat the water up to the given temperature or cool it down from a higher temperature. In this case, water and vapour are in *real* equilibrium. On the other hand, water in contact with hydrogen and oxygen at the ordinary temperature is a case only of *apparent* equilibrium; on changing the pressure and temperature continuously within certain limits there is no continuous change observed in the relative amounts of the two gases. On heating beyond these limits there is a sudden and not a continuous change, and the system no longer regains its former condition on being cooled to the ordinary temperature. In all such cases the system may be regarded as undergoing change and as tending towards a state of true or real equilibrium, but with such slowness that no change is observed.

Although the case of water in contact with hydrogen and oxygen is an extreme one, it must be borne in mind that the condition of true equilibrium may not be reached instantaneously or even with measurable velocity, and in all cases it is necessary to be on one's guard against mistaking apparent (or false) for real (or true) equilibrium. The importance of this will be fully illustrated in the sequel.

CHAPTER II

THE PHASE RULE

ALTHOUGH the fact that chemical reactions do not take place completely in one direction, but proceed only to a certain point and there make a halt, was known in the last quarter of the eighteenth century (Wenzel, 1777; Berthollet, 1799); and although the opening and subsequent decades of the following century brought many further examples of such equilibria to our knowledge, it was not until the last quarter of the nineteenth century that a theorem, general in its application and with foundations weakened by no hypothetical assumptions as to the nature or constitution of matter, was put forward by Willard Gibbs;[1] a generalization which serves at once as a golden rule by which the condition of equilibrium of a system can be tested, and as a guide to the similarities and dissimilarities existing in different systems.

Before that time, certainly, attempts had been made to bring the different known cases of equilibria—chemical and physical—under general laws. From the very first, both Wenzel[2] and Berthollet[3] recognized the influence exercised by the *mass* of the substances on the equilibrium of the system. It was reserved, however, for Guldberg and Waage, by their more general statement and mathematical treatment of the Law of Mass Action,[4] to inaugurate the period of quantitative study of equilibria. The law which these investigators enunciated served satisfactorily to summarize the conditions of equilibrium in many cases both of homogeneous and, with the help of certain assumptions and additions, of heterogeneous equilibrium. By reason, however, of the fact that it was developed on the basis of the kinetic and molecular theories, and involved, therefore, certain hypothetical assumptions as to the nature and condition of the substances taking part in the equilibrium, the law of mass action failed, as it necessarily must, when applied to those systems in which neither the number of different molecular aggregates nor the degree of their molecular complexity was known.

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[1] *Trans. Connecticut Acad.*, 1874–1878.

[2] Lehre von der chemischen Verwandtschaft der Körper, 1777.

[3] See Ostwald's *Klassiker*, No. 74.

[4] Etudes sur les affinités chimiques, 1867; Ostwald's *Klassiker*, No. 104.

The Phase Rule.—Ten years after the law of mass action was propounded by Guldberg and Waage, Willard Gibbs,[1] Professor of Physics in Yale University, showed how, in a perfectly general manner, free from all hypothetical assumptions as to the molecular condition of the participating substances, all cases of equilibrium could be surveyed and grouped into classes, and how similarities in the behaviour of apparently different kinds of systems, and differences in apparently similar systems, could be explained.

As the basis of his theory of equilibria, Gibbs adopted the laws of thermodynamics,[2] a method of treatment which had first been employed by Horstmann.[3] In deducing the law of equilibrium, Gibbs regarded a system as possessing only three independently variable factors[4]—temperature, pressure, and the concentration of the components of the system—and he enunciated the general theorem now usually known as the Phase Rule, by which he defined the conditions of equilibrium as a relationship between the number of what are called the phases and the components of the system.

Phases.—Before proceeding farther we shall first consider what exactly is meant by the terms *phase* and *component*. We have already seen (p. 5) that a heterogeneous system is made up of different portions, each in itself homogeneous, but marked off in space and separated from the other portions by bounding surfaces. These homogeneous, physically distinct and mechanically separable portions are called *phases*. Thus ice, water, and vapour, are three phases of the same chemical substance—water. A phase, however, whilst it must be physically and chemically homogeneous, need not necessarily be chemically simple. Thus, a gaseous mixture or a solution may form a phase; but a heterogeneous mixture of solid substances constitutes as many phases as there are substances present. Thus when calcium carbonate dissociates under the influence of heat, calcium oxide and carbon dioxide are formed. There are then *two* solid phases present, viz. calcium carbonate and oxide, and one gas phase, carbon dioxide.

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[1] Died April, 1903.

[2] For a mathematical treatment of the Phase Rule the reader is referred to the volume in this series on Thermodynamics, by Dr. F. G. Donnan.

[3] Liebig's *Annalen*, 1873, **170**, 192; Ostwald, *Lehrbuch*, II. 2. 111.

[4] The action of gravity and other forces being excluded (see p. 5).

The *number of phases* which can exist side by side may vary greatly in different systems. In all cases, however, there can be but one gas or vapour phase on account of the fact that all gases are miscible with one another in all proportions. In the case of liquid and solid phases the number is indefinite, since the above property does not apply to them. The number of phases which can be formed by any given substance or group of substances also differs greatly, and in general increases with the number of participating substances. Even in the case of a single substance, however, the number may be considerable; in the case of sulphur, for example, at least eight different solid phases are known (*v.* Chap. III.).

It is of importance to bear in mind that equilibrium is *independent of the amounts* of the phases present.[1] Thus it is a familiar fact that the pressure of a vapour in contact with a liquid (*i.e.* the pressure of the saturated vapour) is unaff by the amounts, whether relative or absolute, of the liquic vapour; also the amount of a substance dissolved by a l is independent of the amount of solid in contact wit solution. It is true that deviations from this general law when the amount of liquid or the size of the solid partic reduced beyond a certain point,[1] owing to the influen surface energy; but we have already (p. 5) excluded cases from consideration.

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[1] It may seem as if this were a contradiction to what was said on p. 4 as to the effect of the addition of ammonia or hydrogen chloride to the system constituted by solid ammonium chloride in contact with its products of dissociation. There is, however, no contradiction, because in the case of ammonium chloride the gaseous phase consists of ammonia and hydrogen chloride in equal proportions, and in adding ammonia or hydrogen chloride alone we are not adding the gaseous phase, but only a constituent of it. Addition of ammonia and hydrogen chloride together in the proportions in which they are combined to form ammonium chloride would cause no change in the equilibrium.

Components.—Although the conception of phases i which is readily understood, somewhat greater difficu experienced when we come to consider what is meant l term *component;* for the components of a system are not nymous with the chemical elements or compounds pı *i.e.* with the *constituents* of the system, although both ele and compounds may be components. By the latter term are meant only those constituents the concentration of can undergo *independent* variation in the different phase it is only with these that we are concerned here.[2]

To understand the meaning of this term we shall cc briefly some cases with which the reader will be familia at the outset it must be emphasized that the Phase J concerned merely with those constituents which take ı the state of real equilibrium (p. 5); for it is only to th state, not to the processes by which that state is reache the Phase Rule applies.

Consider now the case of the system water—vapour o water—vapour. The number of constituents taking part equilibrium here is only one, viz. the chemical substance, Hydrogen and oxygen, the constituents of water, are not regarded as components, because, in the first place, th not present in the system in a state of real equilibrium (p. 6); in the second place, they are combined in definite proportions to form water, and their amounts, therefore, cannot be varied independently. A variation in the amount of hydrogen necessitates a definite variation in the amount of oxygen.

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[1] The vapour pressure of water in small drops is greater than water in mass, and the solubility of a solid is greater when in a fine subdivision than when in large pieces (*cf.* Hulett, *Zeitschr. p Chem.*, 1901, **37.** 385).

[2] See Ostwald, *Lehrbuch*, II. **2.** 476, 934; Roozeboom, *Z physikal. Chem.*, 1894, **15.** 150; *Heterogene Gleichgewichte*, I. p. 16 scheider, *Zeitschr. physikal. Chem.*, 1903, **43.** 89.

In the case, already referred to, in which hydrogen and oxygen are present along with water at the ordinary temperature, we are not dealing with a condition of true equilibrium. If, however, the temperature is raised to a certain point, a state of true equilibrium between hydrogen, oxygen, and water-vapour will be possible. In this case hydrogen and oxygen will be components, because now they do take part in the equilibrium; also, they need no longer be present in definite proportions, but excess of one or the other may be added. Of course, if the restriction be arbitrarily made that the free hydrogen and oxygen shall be present always and only in the proportions in which they are combined to form water, there will be, as before, only one component, water. From this, then, we see that a change in the conditions of the experiment (in the present case a rise of temperature) may necessitate a change in the number of the components.

It is, however, only in the case of systems of more than one component that any difficulty will be found; for only in this case will a choice of components be possible. Take, for instance, the dissociation of calcium carbonate into calcium oxide and carbon dioxide. At each temperature, as we have seen, there is a definite state of equilibrium. When equilibrium has been established, there are three different substances present—calcium carbonate, calcium oxide, and carbon dioxide; and these are the constituents of the system between which equilibrium exists. Now, although these constituents take part in the equilibrium, they are not all to be regarded as components, for they are not mutually independent. On the contrary, the different phases are related to one another, and if *two* of these are taken, the composition of the third is defined by the equation

$$CaCO_3 = CaO + CO_2$$

Now, in deciding the number of components in any given system, not only must the constituents chosen be capable of independent variation, but a further restriction is imposed, and we obtain the following rule: *As the components of a system there are to be chosen the* **smallest number** *of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*

Applying this rule to the case under consideration, we see that of the three constituents present when the system is in a state of equilibrium, only two, as already stated, are independently variable. It will further be seen that in order to express the composition of each phase present, two of these constituents are necessary. The system is, therefore, one of *two components*, or a system of the second order.

When, now, we proceed to the actual choice of components, it is evident that any two of the constituents can be selected. Thus, if we choose as components $CaCO_3$ and CaO, the composition of each phase can be expressed by the following equations :—

$$\begin{aligned} CaCO_3 &= CaCO_3 + 0CaO \\ CaO &= CaO + 0CaCO_3 \\ CO_2 &= CaCO_3 - CaO \end{aligned}$$

As we see, then, both zero and negative quantities of the components have been introduced; and similar expressions would be obtained if $CaCO_3$ and CO_2 were chosen as components. The matter can, however, be simplified and the use of negative quantities avoided if CaO and CO_2 are chosen; and it is, therefore, customary to select these as the components.

While it is possible in the case of systems of the second order to choose the two components in such a way that the composition of each phase can be expressed by positive quantities of these, such a choice is not always possible when dealing with systems of a higher order (containing three or four components).

From the example which has just been discussed, it might appear as if the choice of the components was rather arbitrary. On examining the point, however, it will be seen that the arbitrariness affects only the *nature*, not the *number*, of the components; a choice could be made with respect to which, not to how many, constituents were to be regarded as components. As we shall see presently, however, it is only the number, not the nature of the components that is of importance.

After the discussion of the conditions which the substances chosen as components must satisfy, another method may be given by which the number of components present in a system can be determined. Suppose a system consisting of several phases in equilibrium, and the composition of each phase determined by analysis. If each phase present, regarded as a whole, has the same composition, the system contains only one component, or is of the first order. If two phases must be mixed in suitable quantities in order that the composition of a third phase may be obtained, the system is one of two components or of the second order; and if three phases are necessary to give the composition of a fourth coexisting phase, the system is one of three components, or of the third order.[1]

Although the examples to be considered in the sequel will afford sufficient illustration of the application of the rules given above, one case may perhaps be discussed to show the application of the method just given for determining the number of components.

Consider the system consisting of Glauber's salt in equilibrium with solution and vapour. If these three phases are analyzed, the composition of the solid will be expressed by $Na_2SO_4, 10H_2O$; that of the solution by $Na_2SO_4 + xH_2O$, while the vapour phase will be H_2O. The system evidently cannot be a one-component system, for the phases have not all the same composition. By varying the amounts of two phases, however (*e.g.* $Na_2SO_4, 10H_2O$ and H_2O), the composition of the third phase—the solution—can be obtained. The system is, therefore, one of *two components*.

But sodium sulphate can also exist in the anhydrous form and as the hydrate $Na_2SO_4, 7H_2O$. In these cases there may

[1] Ostwald, *Lehrbuch*, II. 2. 478.

be chosen as components Na_2SO_4 and H_2O, and Na_2SO_4, 7H and H_2O respectively. In both cases, therefore, there are t *components.* But the two systems (Na_2SO_4, $10H_2O$—H_2O, a Na_2SO_4, $7H_2O$—H_2O) can be regarded as special cases of t system Na_2SO_4—H_2O, and these two components will app to all systems made up of sodium sulphate and water, matter whether the solid phase is anhydrous salt or one of th hydrates. In all three cases, of course, the *number* of com ponents is the same; but by choosing Na_2SO_4 and H_2O components, the possible occurrence of negative quantities components in expressing the composition of the phases avoided; and, further, these components apply over a mu larger range of experimental conditions. Again, therefo we see that, although the number of the components of system is definite, a certain amount of liberty is allowed in t choice of the substances; and we also see that the choice w be influenced by the conditions of experiment.

Summing up, now, we may say—

(1) The components are to be chosen from among the co stituents which are present when the system is in a state of tr equilibrium, and which take part in that equilibrium.

(2) As components are to be chosen the *smallest num* of such constituents necessary to express the composition each phase participating in the equilibrium, zero and negati quantities of the components being permissible.

(3) In any given system the *number* of the components definite, but may alter with alteration of the conditions experiment. A certain freedom of choice, however, is allow in the (qualitative, not quantitative) selection of the com nents, the choice being influenced by considerations of si plicity, suitability, or generality of application.[1]

Degree of Freedom. Variability of a System.—It is w known that in dealing with a certain mass of gas or vapour, water vapour, if only one of the independently variable fact —temperature, pressure, and concentration (or volume)- fixed, the state of the gas or vapour is undefined; while oc pying the same volume (the concentration, therefore, remain unchanged), the temperature and the pressure may be altered; at a given temperature, a gas can exist under different pressures and occupy different volumes, and under any given pressure the temperature and volume may vary. If, however, two of the factors are arbitrarily fixed, then the third factor can only have a certain definite value; at any given values of temperature and pressure a given mass of gas can occupy only a definite volume.

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[1] See also Hoitsema, *Zeitschr. physikal. Chem.* 1895, **17**. 651.

Suppose, however, that the system consists of water in contact with vapour. The condition of the system then becomes perfectly defined on arbitrarily giving one of the variables a certain value. If the temperature is fixed, the pressure under which water and water vapour can coexist is also determined; and conversely, if a definite pressure is chosen, the temperature is also defined. Water and vapour can coexist under a given pressure only at a definite temperature.

Finally, let the water and vapour be cooled down until ice begins to separate out. So soon as the third phase, ice, appears, the state of the system as regards temperature and pressure of the vapour is perfectly defined, and none of the variables can be arbitrarily changed without causing the disappearance of one of the phases, ice, water, or vapour.

We see, therefore, that in the case of some systems two, in other cases, only one of the independent variables (temperature, pressure, concentration) can be altered without destroying the nature of the system; while in other systems, again, these variables have all fixed and definite values. We shall therefore define the number of degrees of freedom[1] of a system as the *number of the variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.* From what has been said, therefore, we shall describe a gas or vapour as having two degrees of freedom; the system water—vapour as having only one; and the system ice—water—vapour as having no degrees of freedom. We may also speak of the

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[1] The term "degree of freedom" employed here must not be confused with the same term used to denote the various movements of a gas molecule according to the kinetic theory.

variability or *variance* of a system, and describe a system as being invariant, univariant, bivariant, multivariant,[1] according as the number of degrees of freedom is nought, one, two, or more than two.

A knowledge of its variability is, therefore, of essential importance in studying the condition and behaviour of a system, and it is the great merit of the Phase Rule that *the state of a system is defined entirely by the relation existing between the number of the components and the phases present*, no account being taken of the molecular complexity of the participating substances, nor any assumption made with regard to the constitution of matter. It is, further, as we see, quite immaterial whether we are dealing with "physical" or "chemical" equilibrium; in principle, indeed, no distinction need be drawn between the two classes; although it is nevertheless often convenient to make use of the terms, in spite of a certain amount of indefiniteness which attaches to them—an indefiniteness, indeed, which attaches equally to the terms "physical" and "chemical" process.[2]

The *Phase Rule* of Gibbs, now, which defines the conditions of equilibrium by the relation between the number of coexisting phases and the components, may be stated as follows: A system consisting of n components can exist in $n + 2$ phases only when the temperature, pressure, and concentration have fixed and definite values; if there are n components in $n + 1$ phases, equilibrium can exist while one of the factors varies, and if there are only n phases, two of the varying factors may be arbitrarily fixed. This rule, the application of which, it is hoped, will become clear in the sequel, may be very concisely and conveniently summarized in the form of the equation—

$$P + F = C + 2, \text{ or } F = C + 2 - P$$

where P denotes the number of the phases, F the degrees of freedom, and C the number of components. From the second form of the equation it can be readily seen that the greater the number of the phases, the fewer are the degrees of freedom. With increase in the number of the phases, therefore, t condition of the system becomes more and more defined, or less and less variable.

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[1] Trevor, *Jour. Physical Chem.*, 1902, 6, 136.

[2] Ostwald, *Principles of Inorganic Chemistry*, p. 7. (Macmillan.)

Classification of Systems according to the Phase Rule. —We have already learned in the introductory chapter that systems which are apparently quite different in character may behave in a very similar manner. Thus it was stated that the laws which govern the equilibrium between water and its vapour are quite analogous to those which are obeyed by the dissociation of calcium carbonate into carbon dioxide and calcium oxide; in each case a certain temperature is associated with a definite pressure, no matter what the relative or absolute amounts of the respective substances are. And other examples were given of systems which were apparently similar in character, but which nevertheless behaved in a different manner. The relations between the various systems, however, become perfectly clear and intelligible in the light of the Phase Rule. In the case first mentioned, that of water in equilibrium with its vapour, we have one component—water—present in two phases, *i.e.* in two physically distinct forms, viz. liquid and vapour. According to the Phase Rule, therefore, since $C = 1$, and $P = 2$, the degree of freedom F is equal to $1 + 2 - 2 = 1$; the system possesses one degree of freedom, as has already been stated. But in the case of the second system mentioned above there are two components, viz. calcium oxide and carbon dioxide (p. 12), and three phases, viz. two solid phases, CaO and $CaCO_3$, and the gaseous phase, CO_2. The number of degrees of freedom of the system, therefore, is $2 + 2 - 3 = 1$; this system, therefore, also possesses one degree of freedom. We can now understand why these two systems behave in a similar manner; both are univariant, or possess only one degree of freedom. We shall therefore expect a similar behaviour in the case of all univariant systems, no matter how dissimilar the systems may otherwise appear. Similarly, all bivariant systems will exhibit analogous behaviour; and generally, systems possessing the same degree of freedom will show a like behaviour. In accordance with the Phase Rule, therefore, we may classify the different systems which may be found into invariant, univariant, bivariant, multivariant, represented by BO (ice and vapour), and OA (water and vapour) is the vapour phase; and the area BOA is therefore the area of the vapour phase. Similarly, BOC is the area of the ice phase, and COA the area of the water phase.

Supercooled Water. Metastable State.—When heated under the ordinary atmospheric pressure, ice melts when the temperature reaches 0°, and it has so far not been found possible to raise the temperature of ice above this point without liquefaction taking place. On the other hand, it has long been known that water can be cooled below zero without solidification occurring. This was first discovered in 1724 by Fahrenheit,[1] who found that water could be exposed to a temperature of −9·4° without solidifying; so soon, however, as a small particle of ice was brought in contact with the water, crystallization commenced. Superfused or supercooled water—*i.e.* water cooled below 0°—is unstable only in respect of the solid phase; so long as the presence of the solid phase is carefully avoided, the water can be kept for any length of time without solidifying, and the system supercooled water and vapour behaves in every way like a stable system. A system, now, which in itself is stable, and which becomes instable only in contact with a particular phase, is said to be *metastable*, and the region throughout which this condition exists is called the metastable region. Supercooled water, therefore, is in a metastable condition. If the supercooling be carried below a certain temperature, solidification takes place spontaneously without the addition of the solid phase; the system then ceases to be metastable, and becomes *instable*.

Not only has water been cooled to temperatures considerably below the melting point of ice, but the vapour pressure of the supercooled water has been measured. It is of interest and importance, now, to see what relationship exists between the vapour pressure of ice and that of supercooled water at the same temperature. This relationship is clearly shown by the

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than two right angles. It may be useful to remember that an invariant system is represented by a *point*, a univariant system by a *line*, and a bivariant system by an *area*.

[1] *Phil. Trans.*, 1724, **39**. 78.

numbers in the following table,[1] and is represented in Fig. 3, p. 25, and diagrammatically in Fig. 4, the vapour pressures of supercooled water being represented by the curve OA′, which is the unbroken continuation of AO.

VAPOUR PRESSURE OF ICE AND OF SUPERCOOLED WATER.

Temperature.	Pressure in mm. mercury.		
	Water.	Ice.	Difference.
0°	4·618	4·602	0·016 *
−2°	3·995	3·925	0·070
−4°	3·450	3·334	0·116
−8°	2·558	2·379	0·179
−10°	2·197	1·999	0·198
−15°	1·492	1·279	0·213
−20°	1·005	0·806	0·199

At all temperatures below 0° (more correctly +0·0076°), at which temperature water and ice have the same vapour pressure, the vapour pressure of supercooled water is *greater* than that of ice at the same temperature.

From the relative positions of the curves OB and OA (Fig. 4) we see that at all temperatures above 0°, the (metastable) sublimation curve of ice, if it could be obtained, would be higher than the vaporization curve of water. This shows, therefore, that at 0° a "break" must occur in the curve of states, and that in the neighbourhood of this break the curve above that point must ascend less rapidly than the curve below the break. Since, however, the differences in the vapour pressures of supercooled water and of ice are very small, the change in the direction of the vapour-pressure curve on passing from ice to water was at first not observed, and Regnault regarded the sublimation curve as passing continuously into the vaporization curve. The existence of a break was, however, shown by James Thomson[1] and by Kirchhoff[2] to be demanded by thermo-dynamical considerations, and the prediction of theory was afterwards realized experimentally by Ramsay and Young in their determinations of the vapour pressure of water and ice, as well as in the case of other substances.[3]

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[1] Juhlin, *loc. cit.*, p. 61; cf. Ramsay and Young, *loc. cit.*: Thiesen and Scheel, *loc. cit.*

* This small difference is due to experimental errors in the determination of the vapour pressures; a differential method betrayed no difference between the vapour pressure of ice and of water at 0°.

From what has just been said, we can readily understand why ice and water cannot exist in equilibrium below 0°. For, suppose we have ice and water in the same closed space, but not in contact with one another, then since the vapour pressure of the supercooled water is higher than that of ice, the vapour of the former must be supersaturated in contact with the latter; vapour must, therefore, condense on the ice; and in this way there will be a slow distillation from the water to the ice, until at last all the water will have disappeared, and only ice and vapour remain.[4]

Other Systems of the Substance Water.—We have thus far discussed only those systems which are constituted by the three phases—ice, water, and water vapour. It has, however, been recently found that at a low temperature and under a high pressure ordinary ice can pass into two other crystalline varieties, called by Tammann[5] ice II. and ice III., ordinary ice being ice I. According to the Phase Rule, now, since each of these solid forms constitutes a separate phase (p. 9), it will be possible to have the following (and more) systems of water, in addition to those already studied, viz. water, ice I., ice II.; water, ice I., ice III.; water, ice II., ice III., forming invariant systems and existing in equilibrium only at a definite triple point; further, water, ice II.; water, ice III.; ice I., ice II.; ice I., ice III.; ice II., ice III., forming univariant systems, existing, therefore, at definite corresponding values of by Ramsay and Young, while the values of the critical pressure and temperature are those determined by Battelli.[1]

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[1] *Phil. Mag.*, 1874 [4], **47**. 447; *Proc. Roy. Soc.*, 1873, **22**. 27.

[2] *Pogg. Annalen*, 1858, **103**, 206.

[3] See *Phil. Trans.*, 1884, **175**, 461.

[4] This phenomenon of distillation from the supercooled liquid to the solid has been very clearly observed in the case of furfuraldoxime (V Goldschmidt, *Zeitschr. f. Krystallographie*, 1897, **28**. 169).

[5] *Annalen der Physik*, 1900 [4], **2**. 1, 424.

VAPOUR PRESSURE OF WATER.

Temperature.	Pressure in cm. mercury.	Temperature.	Pressure in cm. mercury.
−10°	0·213	120°	148·4
0°	0·458*	130°	201·9
+20°	1·752	150°	356·8
40°	5·516	200°	1162·5
60°	14·932	250°	2973·4
80°	35·54	270°	4110·1
100°	76·00	364·3° (critical temperature)	14790·4 (194·6 atm.) (critical pressure).

The pressure is, of course, independent of the relative or absolute volumes of the liquid and vapour; on increasing the volume at constant temperature, a certain amount of the liquid will pass into vapour, and the pressure will regain its former value. If, however, the pressure be permanently maintained at a value different from that corresponding to the temperature employed, then either all the liquid will pass into vapour, or all the vapour will pass into liquid, and we shall have either vapour alone or liquid alone.

Upper Limit of Vaporization Curve.—On continuing to add heat to water contained in a closed vessel, the pressure of the vapour will gradually increase. Since with increase of pressure the density of the vapour must increase, and since with rise of temperature the density of the liquid must decrease, a point will be reached at which the density of liquid and vapour become identical; the system ceases to be heterogeneous, and passes into one homogeneous phase. The temperature at which this occurs is called the *critical temperature.* To this temperature there will, of course, correspond a certain definite pressure, called the *critical pressure.* The curve representing the

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[1] *Annales chim. et phys.*, 1892 [6], **26**. 425.

* The vapour pressure of water at 0° has recently been very accurately determined by Thiesen and Scheel (*loc. cit.*), and found to be 4·579 ± 0·001 mm. of mercury (at 0°), or equal to 0·006025 atm.

Sulphur exists in two well-known crystalline forms—rhombic, or octahedral, and monoclinic, or prismatic sulphur. Of these, the former melts at 114·5°; the latter at 120°.[1] Further, at the ordinary temperature, rhombic sulphur can exist unchanged, whereas, on being heated to temperatures somewhat below the melting point, it passes into the prismatic variety. On the other hand, at temperatures above 96°, prismatic sulphur can remain unchanged, whereas at the ordinary temperature it passes slowly into the rhombic form.

If, now, we examine the case of sulphur with the help of the Phase Rule, we see that the following systems are theoretically possible :—

I. *Bivariant Systems : One component in one phase.*
- (*a*) Rhombic sulphur.
- (*b*) Monoclinic sulphur.
- (*c*) Sulphur vapour.
- (*d*) Liquid sulphur.

II. *Univariant Systems : One component in two phases.*
- (*a*) Rhombic sulphur and vapour.
- (*b*) Monoclinic sulphur and vapour.
- (*c*) Rhombic sulphur and liquid.
- (*d*) Monoclinic sulphur and liquid.
- (*e*) Rhombic and monoclinic sulphur.
- (*f*) Liquid and vapour.

III. *Invariant Systems : One component in three phases.*
- (*a*) Rhombic and monoclinic sulphur and vapour.
- (*b*) Rhombic sulphur, liquid and vapour.
- (*c*) Monoclinic sulphur, liquid and vapour.
- (*d*) Rhombic and monoclinic sulphur and liquid.

Triple Point—Rhombic and Monoclinic Sulphur and Vapour. Transition Point.—In the case of ice, water and vapour, we saw that at the triple point the vapour pressures of ice and water are equal; below this point, ice is stable; above this point, water is stable. We saw, further, that below 0° the vapour pressure of the stable system is lower than that of the metastable, and therefore that at the triple point there is a break in the vapour pressure curve of such a kind that above

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[1] Brodie, *Proc. Roy. Soc.*, 1855, 7. 24.

VAPOUR PRESSURE OF ICE.

Temperature.	Pressure in mm. mercury.	Temperature.	Pressure in mm. mercury.
−50°	0·050	−8°	2·379
−40°	0·121	−6°	2·821
−30°	0·312	−4°	3·334
−20°	0·806	−2°	3·925
−15°	1·279	0°	4·602
−10°	1·999		

Equilibrium between Ice and Water. Curve of Fusion.—There is still another univariant system of the one component water, the existence of which, at definite values of temperature and pressure, the Phase Rule allows us to predict. This is the system solid—liquid. Ice on being heated to a certain temperature melts and passes into the liquid state; and since this system solid—liquid is univariant, there will be for each temperature a certain definite pressure at which ice and water can coexist or be in equilibrium, independently of the amounts of the two phases present. Since now the temperature at which the solid phase is in equilibrium with the liquid phase is known as the melting point or point of fusion of the solid, the curve representing the temperatures and pressures at which the solid and liquid are in equilibrium will represent the change of the melting point with the pressure. Such a curve is called the *curve of fusion*, or the melting-point curve.

It was not until the middle of the nineteenth century that this connection between the pressure and the melting point, or the change of the melting point with the pressure, was observed. The first to recognize the existence of such a relationship was James Thomson,[1] who in 1849 showed that from theoretical considerations such a relationship must exist, and predicted that in the case of ice the melting point would be lowered by pressure. This prediction was fully confirmed by his brother, W. Thomson[2] (Lord Kelvin), who found that under a pressure of 8·1 atm. the melting point of ice was −0·059°; under a pressure of 16·8 atm. the melting point was −0·129°.

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[1] *Trans. Roy. Soc. Edin.*, 1849, **16**. 575.

[2] *Proc. Roy. Soc. Edin.*, 1850, **2**, 267.

The experiments which were first made in this connection were more of a qualitative nature, but in recent years careful measurements of the influence of pressure on the melting point of ice have been made more especially by Tammann,[1] and the results obtained by him are given in the following table and represented graphically in Fig. 2.

Fusion Pressure of Ice.

Temperature.	Pressure in kilogms. per sq. cm.[2]	Change of melting point for an increase of pressure of 1 kilogm. per sq. cm.
−0°	1	0·0074°
−2·5°	336	0·0090°
−5°	615	0·0091°
−7·5°	890	0·0094°
−10·0°	1155	0·0100°
−12·5°	1410	0·0116°
−15·0°	1625	0·0119°
−17·5°	1835	0·0121°
−20·0°	2042	0·0133°
−22·1°	2200	

From the numbers in the table and from the figure we see that as the pressure is increased the melting point of ice is lowered; but we also observe that a very large change of pressure is required in order to produce a very small change in the melting point. The curve, therefore, is very steep. Increase of pressure by one atmosphere lowers the melting point by only 0·0076°,[3] or an increase of pressure of 135 atm. is required to produce a lowering of the melting point of 1°. We see further that the fusion curve bends slightly as the pressure is increased, which signifies that the variation of the melting point with the pressure changes; at −15°, when the pressure is 1625 kilogm. per sq. cm., increase of pressure

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[1] *Annalen der Physik*, 1899 [3], **68**. 564; 1900 [4], **2**. 1, 424. See also Dewar, *Proc. Roy. Soc.*, 1880, **30**. 533.

[2] The pressure of 1 atmosphere is equal to 1·033 kilogm. per sq. cm.; or the pressure of 1 kilogm. per sq. cm. is equal to 0·968 atm.

[3] Tammann, *loc. cit.*, 1900, **2**. 1, 424; cf. Goossens, *Arch. néerland.*, 1886, **20**. 449.

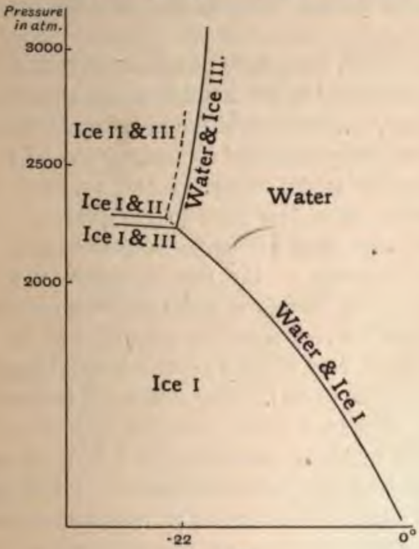

FIG. 2

by 1 kilogm. per sq. cm. lowers the melting point by 0·012°. This curvature of the fusion curve we shall later (Chap. IV.) see to be an almost universal phenomenon.

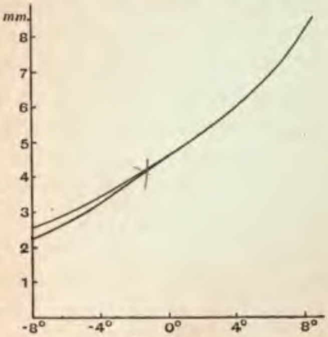

FIG. 3.

Equilibrium between Ice, Water, and Vapour. The Triple Point.—On examining the vapour-pressure curves of ice and water (Fig. 3), we see that at a temperature of about 0° and under a pressure of about 4·6 mm. mercury, the two curves t. At this point liquid water solid ice are each in equi- um with vapour at the same re. Since this is so, they must, of course, be in equilibrium

Triple Point—Monoclinic Sulphur, Liquid, and Vapour. Melting Point of Monoclinic Sulphur.—Above 95·5°, monoclinic sulphur is, as we have seen, the stable form. On being heated to 120°, under atmospheric pressure, it melts. This temperature is, therefore, the point of equilibrium between monoclinic sulphur and liquid sulphur under atmospheric pressure. Since we are dealing with a condensed system, this temperature may be regarded as very nearly that at which the solid and liquid are in equilibrium with their vapour, *i.e.* the triple point, solid (monoclinic)—liquid—vapour. This point is represented in the diagram by B.

Triple Point—Rhombic and Monoclinic Sulphur and Liquid.—In contrast with that of ice, the fusion point of monoclinic sulphur is *raised* by increase of pressure, and the fusion curve, therefore, slopes to the right. The transition curve of rhombic and monoclinic sulphur, as we have seen, also slopes to the right, and more so than the fusion curve of monoclinic sulphur. There will, therefore, be a certain pressure and temperature at which the two curves will cut. This point lies at 151°, and a pressure of 1320 kilogm. per sq. cm., or about 1288 atm.[1] It, therefore, forms another triple point, the existence of which had been predicted by Roozeboom,[2] at which rhombic and monoclinic sulphur are in equilibrium with liquid sulphur. It is represented in our diagram by the point C. *Beyond this point monoclinic sulphur ceases to exist in a stable condition.* At temperatures and pressures above this triple point, rhombic sulphur will be the stable modification, and this fact is of mineralogical interest, because it explains the occurrence in nature of well-formed rhombic crystals. Under ordinary conditions, prismatic sulphur separates out on cooling fused sulphur, but at temperatures above 151° and under pressures greater than 1288 atm., the rhombic form would be produced.[3]

Triple Point—Rhombic Sulphur, Liquid, and Vapour. Metastable Triple Point.—On account of the slowness with hich transformation of one form into the other takes place on assing the transition point, it has been found possible to heat hombic sulphur up to its melting point (114·5°). At this emperature, not only is rhombic sulphur in a metastable condition, but the liquid is also metastable, its vapour pressure being greater than that of solid monoclinic sulphur. This point is represented in our diagram by the point *b*.

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[1] Tammann, *Annalen der Physik*, 1899 [3], **68**. 633.

[2] *Rec. Trav. Chim. Pays-Bas*, 1887, **6**. 314.

[3] *Cf.* van't Hoff, *Lectures on Physical Chemistry*, I., p. 27 (Arnold).

From the relative positions of the metastable melting point of rhombic sulphur and the stable melting point of monoclinic sulphur at 120°, we see that, of the two forms, the metastable form has the lower melting point. This, of course, is valid only for the relative stability in the neighbourhood of the melting point; for we have already learned that at lower temperatures rhombic sulphur is the stable, monoclinic sulphur the metastable (or unstable) form.

Fusion Curve of Rhombic Sulphur.—Like any other melting point, that of rhombic sulphur will be displaced by increase of pressure; increase of pressure raises the melting point, and we can therefore obtain a metastable fusion curve representing the conditions under which rhombic sulphur is in equilibrium with liquid sulphur. This metastable fusion curve must pass through the triple point for rhombic sulphur—monoclinic sulphur—liquid sulphur, and on passing this point it becomes a stable fusion curve. The continuation of this curve, therefore, above 151° forms the stable fusion curve of rhombic sulphur (curve CD).

These curves have been investigated at high pressures by Tammann, and the results are represented according to scale in Fig. 6,[1] *a* being the curve for monoclinic sulphur and liquid; *b*, that for rhombic sulphur and liquid; and *c*, that for rhombic and monoclinic sulphur.

Bivariant Systems.—Just as in the case of the diagram of states of water, the areas in Fig. 5 represent the conditions for the stable existence of the single phases: rhombic sulphur in the area to the left of AOCD; monoclinic sulphur in the area OBC; liquid sulphur in the area EBCD; sulphur vapour below the curves AOBE. As can be seen from the diagram, the existence of monoclinic sulphur is limited on all sides, area being bounded by the curves OB, OC, BC. At any p outside this area, monoclinic sulphur can exist only in a m stable condition.

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[1] *Annalen der Physik*, 1899 [3], **68**. 663.

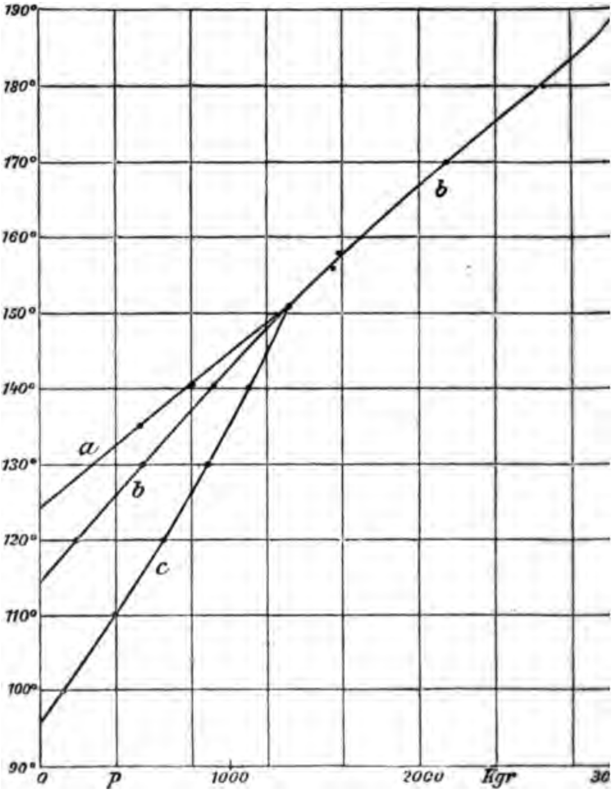

FIG. 6.

Other crystalline forms of sulphur have been obtaine that the existence of other systems of the one-comp sulphur besides those already described is possible. Refe will be made to these later (p. 49).

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[1] Brauns, *Jahrbuch für Mineralogie*, 1899–1901, **13.** Beilage, p. 3

C. *Tin.*

ther substance capable of existing in more than one ine form, is the metal tin, and although the general ur, so far as studied, is analogous to that of sulphur, account of the two varieties of tin may be given ot only on account of their metallurgical interest, on account of the importance which the phenomena for the employment of this metal in everyday life.

r a winter of extreme severity in Russia (1867–1868), ewhat unpleasant discovery was made that a number s of tin, which had been stored in the Customs House etersburg, had undergone disintegration and crumbled ey powder.[1] That tin undergoes change on exposure eme cold was known, however, before that time, even back as the time of Aristotle, who spoke of the tin as g."[2] Ludicrous as that term may now appear, Aristotle eless unconsciously employed a strikingly accurate , for the conditions under which ordinary white tin into the grey modification are, in many ways, quite analo- those under which a substance passes from the solid liquid state. The knowledge of this was, however, the wisdom of the Greek philosopher.

many years there existed considerable confusion both he conditions under which the transformation of white its allotropic modification occurs, and to the reason change. Under the guidance of the Phase Rule, how- e confusion which obtained has been cleared away, and ysterious" behaviour of tin brought into accord with henomena of transformation.[3]

nsition Point.—Just as in the case of sulphur, so also case of tin, there is a transition point above which the one form, ordinary white tin, and below which the other form, grey tin, is the stable variety. In the case of this metal, the transition point was found by Cohen and van Eyk, who employed both the dilatometric and the electrical methods (Appendix) to be 20°. Below this temperature, grey tin is the stable form. But, as we have seen in the case of sulphur, the change of the metastable into the stable solid phase occurs with considerable slowness, and this behaviour is found also in the case of tin. Were it not so, we should not be able to use this metal for the many purposes to which it is applied in everyday life; for, with the exception of a comparatively small number of days in the year, the temperature of our climate is below 20°, and *white tin is, therefore, at the ordinary temperature, in a metastable condition.* The change, however, into the stable form at the ordinary temperature, although slow, nevertheless takes place, as is shown by the partial or entire conversion of articles of tin which have lain buried for several hundreds of years.

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[1] itsche, *Ber.*, 1869, **2**. 112, 540.

[2] *e mirabilibus Auscultationibus*, Cap. 51 (*v.* Cohen, *Zeitschr. l. Chem.*, 1901, **36**. 513).

[3] Cohen and C. van Eyk, *Zeitschr. physikal. Chem.*, 1899, **30**. 601; *ibid.*, 1900, **33**. 59; **35**. 588; 1901, **36**. 513.

On lowering the temperature, the velocity with which the transformation of the tin occurs is increased, and Cohen and van Eyk found that the temperature of maximum velocity is about −50°. Contact with the stable form will, of course, facilitate the transformation.

The change of white tin into grey takes place also with increased velocity in presence of a solution of tin ammonium chloride (pink salt), which is able to dissolve small quantities of tin. In presence of such a solution also, it was found that the temperature at which the velocity of transformation was greatest was raised to 0°. At this temperature, white tin in contact with a solution of tin ammonium chloride, and the grey modification, undergoes transformation to an appreciable extent in the course of a few days.

Fig. 7 is a photograph of a piece of white tin undergoing transformation into the grey variety.[1] The bright surface of the tin becomes covered with a number of warty masses, formed of the less dense grey form, and the number and size of these continue to grow until the whole of the white tin has passed ey powder. On account of the appearance which is , this transformation of tin has been called by Cohen plague."

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[1] *Zeitschr. physikal. Chem.*, 1900, **33**, 58.

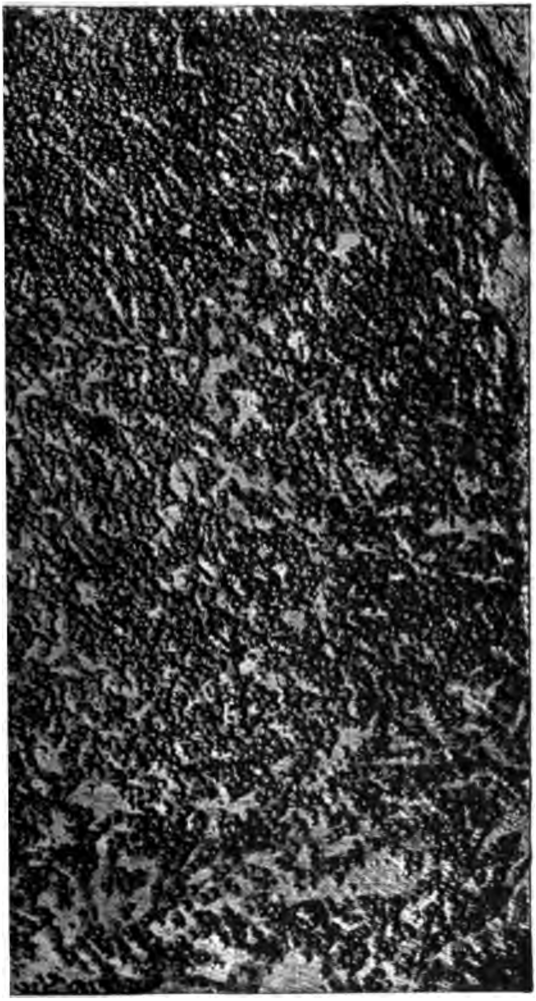

FIG. 7.

Enantiotropy and Monotropy.—In the case of sulphur a tin, we have met with two substances existing in polymorp forms, and we have also learned that these forms exhibi definite transition point at which their relative stability reversed. Each form, therefore, possesses a definite rang stable existence, and is capable of undergoing transforma into the other, at temperatures above or below that of transition point.

Another class of dimorphous substances is, however, with as, for instance, in the case of the well-known compo iodine monochloride and benzophenone. Each cryst form has its own melting point, the dimorphous forms of i monochloride melting at 13·9° and 27·2°,[1] and those of zophenone at 26° and 48°.[2] This class of substance d from that which we have already studied (*e.g.* sulphur and in that at all temperatures up to the melting point, onl of the forms is stable, the other being metastable. is, therefore, no transition point, and transformation o crystalline forms can be observed *only in one direction.* two classes of phenomena are distinguished by the r *enantiotropy* and *monotropy;* enantiotropic substances being that the change of one form into the other is a reversibl cess (*e.g.* rhombic sulphur into monoclinic, and monoc sulphur into rhombic), and monotropic substances, the which the transformation of the crystalline forms is ir sible.

These differences in the behaviour can be explaine well in many cases by supposing that in the case of tiotropic substances the transition point lies below the m point, while in the case of monotropic substances, it lies the melting point.[3] These conditions would be represent the Figs. 8 and 9.

In these two figures, O_3 is the transition point, O O_2 the melting points of the metastable and stable ectively. From Fig. 9 we see that the crystalline form I. ll temperatures up to its melting point is metastable with ect to the form II. In such cases the transition point d be reached only at higher pressures.

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[1] Stortenbeker, *Zeitschr. physikal. Chem.*, 1889, **3.** 11 ; *Rec. Trav.* [illegible] P[illegible]s, 1888, **7.** 152.

[illegible]ke, *Ber.*, 1871, **4.** 576.

[illegible] *Zeitschr. physikal. Chem.*, 1897, **22.** 313.

lthough, as already stated, this explanation suffices for cases, it does not prove that in all cases of monotropy ansition point is above the melting point of the two forms. lso quite possible that the transition point may lie below elting points;[1] in this case we have what is known as *monotropy.* It is possible that graphite and diamond,[2]

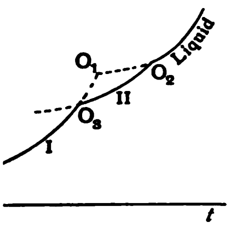

FIG. 8.

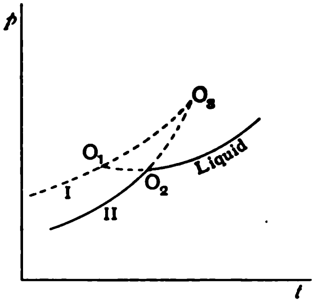

FIG. 9.

ps also the two forms of phosphorus, stand in the relation udomonotropy (*v.* p. 47).

he disposition of the curves in Figs. 8 and 9 also explains henomenon sometimes met with, especially in organic istry, that the substance first melts, then solidifies, and lts at a higher temperature. On again determining the ng point after re-solidification, only the higher melting is obtained.

he explanation of such a behaviour is, that if the determination of the melting point is carried out rapidly, the point the melting point of the metastable solid form, may be zed. At this temperature, however, the liquid is metastable respect to the stable solid form, and if the temperature is not allowed to rise above the melting point of the latter, th liquid may solidify. The stable solid modification thus obtained will melt only at a higher temperature.

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[1] Roozeboom, *Das Heterogene Gleichgewicht,* I. p. 177.

[2] Roozeboom, *ibid.*, p. 179.

D. *Phosphorus.*

An interesting case of a monotropic dimorphous substance is found in phosphorus, which occurs in two crystalline forms; white phosphorus belonging to the regular system, and red phosphorus belonging to the hexagonal system. From determinations of the vapour pressures of liquid white phosphorus, and of solid red phosphorus,[1] it was found that the vapour pressure of red phosphorus was considerably lower than that of liquid white phosphorus at the same temperature, the values obtained being given in the following table.

VAPOUR PRESSURES OF WHITE AND RED PHOSPHORUS.

Vapour pressure of liquid white phosphorus.				Vapour pressure of red phosphorus.	
Temperature.	Pressure in cm.	Temperature.	Pressure in atm.	Temperature.	Pressure in atm.
165°	12	360°	3·2	360°	0·1
180°	20·4	440°	7·5	440°	1·75
200°	26·6	494°	18·0	487°	6·8
219°	35·9	503°	21·9	510°	10·8
230°	51·4	511°	26·2	531°	16·0
290°	76·0	—	—	550°	31·0
—	—	—	—	577°	56·0

These values are also represented graphically in Fig. 10.

At all temperatures above about 260°, transformation of th white into the red modification takes place with appreciab velocity, and this velocity increases as the temperature is raise Even at lower temperatures, *e.g.* at the ordinary temperatur the velocity of transformation is increased under the influenc r by the presence of certain substances, *e.g.* iodine,[2] velocity of transformation of white tin into the grey n was in- the presence n of tin am- loride (p. 40). rdinary tem- erefore, white must be con- he less stable) form, for can exist in h red phos- long period, pressure, as en, is greater of the red n, and also, y in different solvents is greater[3] than that of the ation; as we shall find later, the solubility of the form is always greater than that of the stable.

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[1] Schrötter, *Pogg. Annalen*, 1850, **81**. 276; Troost and Hautefeuill *Annales de Chim. et Phys.* 1874 [5], **2**. 153; *Ann. Scient. École Norm* 1868 [2], II. 266.

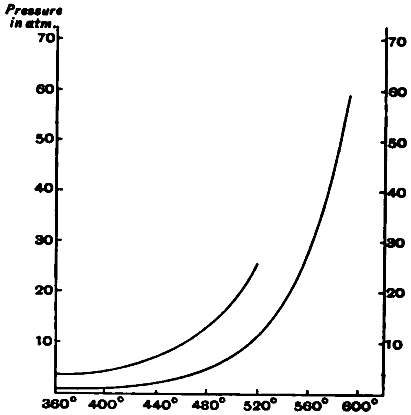

FIG. 10.

ationships which are met with in the case of phos- be best represented by the diagram, Fig. 11.[4]

figure, BO_1 represents the conditions of equilibrium variant system red phosphorus and vapour, which the melting point of red phosphorus. By heating tubes of hard glass, Chapman[5] found that red melts at the melting point of potassium iodide, *i.e.* ,[6] but the pressure at this temperature is unknown.

then, we have the triple point, red phosphorus, vapour, and starting from it, we should have the

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Trans. Chem. Soc., 1890, **57**. 599.

Trans. Chem. Soc., 1853, **5**, 289.

a familiar fact in the case of the solubility in carbon

om, *Das Heterogene Gleichgewicht*, I. p. 170.

Chem. Soc., 1899, **57**. 734.

y, *Trans. Chem. Soc.*, 1876, **29**. 489; 1878, **33**. 275. V.
iddle, *Ber.*, 1893, **26**. 2443.

vaporization curve of liquid phosphorus, O_1A, and the fusio curve of red phosphorus, O_1F. Although these have not bee determined, the latter curve must, from theoretical considera tions (*v.* p. 56), slope slightly to the right; *i.e.* increase o pressure raises the melting point of red phosphorus.

When white phosphorus is heated to 44°, it melts. At thi point, therefore, we shall have another triple point, white pho phorus—liquid—vapour; the pressure at this point has bee calculated to be 3 mm.[1] This point is the intersection o three curves, viz. sublimation curve, vaporization curve, and

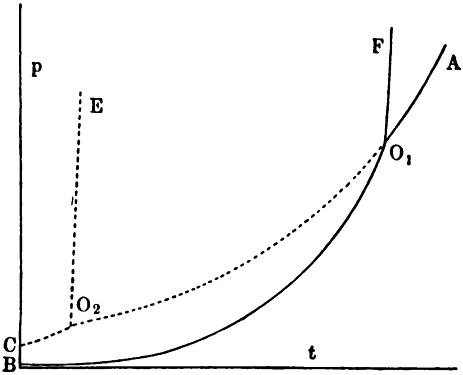

FIG. 11.

the fusion curve of white phosphorus. The fusion curve, O_2 has been determined by Tammann[2] and by G. A. Hulett,[3] an it was found that increase of pressure by 1 atm. raises th melting point by 0·029°. The sublimation curve of white pho phorus has not yet been determined.

As can be seen from the table of vapour pressures (p. 44) the vapour pressure of white phosphorus has been determine up to 500°; at temperatures above this, however, the veloci with which transformation into red phosphorus takes place i so great as to render the determination of the vapour pressu

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[1] Riecke, *Zeitschr. physikal. Chem.*, 1890, **6**. 411.

[2] *Annalen der Physik.*, 1898 [3], **66**. 492.

[3] *Zeitschr. physikal. Chem.*, 1899, **28**. 666.

her temperatures impossible. Since, however, the differ-
between white phosphorus and red phosphorus disappears
liquid state, the vapour pressure curve of white phosphorus
pass through the point O_1, the melting point of red phos-
is, and must be continuous with the curve O_1A, the vapour
ire curve of liquid phosphorus (*vide infra*). Since, as
to shows, the vapour pressure curve of white phosphorus
ds very rapidly at higher temperatures, the "break"
en BO_1 and O_1A must be very slight.

s compared with monotropic substances like benzophenone,
horus exhibits the peculiarity that transformation of the
table into the stable modification takes place with great
ess; and further, the time required for the production of
brium between red phosphorus and phosphorus vapour is
compared with that required for establishing the same
brium in the case of white phosphorus. This behaviour
e best explained by the assumption that change in the
ular complexity (polymerization) occurs in the conversion
ite into red phosphorus, and when red phosphorus passes
apour (depolymerization).[1]

his is borne out by the fact that measurements of the
ır density of phosphorus vapour at temperatures of 500°
nore, show it to have the molecular weight represented
$_4$,[2] and the same molecular weight has been found for
horus in solution.[3] On the other hand, it has recently
shown by R. Schenck,[4] that the molecular weight of red
horus is at least P_8, and very possibly higher.

ı the case of phosphorus, therefore, it is more than pos-
that we are dealing, not simply with two polymorphic

See Naumann, *Ber.*, 1872, **4**. 646; Troost and Hautefeuille, *Compt.*
, **1868**, **66**. 795; 1868, **67**. 1345; Roozeboom, *Das Heterogene Gleich-*
ht, I. pp. 62, 171.

Mitscherlich, *Lieb. Annalen*, 1834, **12**. 137; Deville and Troost,
t. rend., 1863, **56**. 891.

Beckmann, *Zeitschr. physikal. Chem.*, 1890, **5**. 79; Hertz, *ibid.*, **6**.

Ber., 1902, **35**. 351. *Cf.* also, K. Schaum, *Annalen der Chem.*,
, **00**. 221; R. Wegscheider and Kaufler, *Sitzungsber. kaiserl. Akad.*
uch. in Wien, 1901, **110**, II. 606.

forms of the same substance, but with polymeric forms, and that there is no transition point at temperatures above the absolute zero, unless we assume the molecular complexity of the two forms to become the same. The curve for red phosphorus would therefore lie below that of white phosphorus, for the vapour pressure of the polymeric form, if produced from the simpler form with evolution of heat, must be lower than that of the latter. A transition point would, of course, become possible if the sign of the heat effect in the transformation of the one modification into the other should change. If, further, the liquid which is produced by the fusion of red phosphorus at 630° under high pressure also exists in a polymeric form, greater than P_4, then the metastable vaporization curve of white phosphorus would not pass through the melting point of red phosphorus, as was assumed above.[1]

We have already seen in the case of water (p. 29) that the vapour pressure of supercooled water is greater than that of ice, and that therefore it is possible, theoretically at least, by a process of distillation, to transfer the water from one end of a closed tube to the other, and to there condense it as ice. On account of the very small difference between the vapour pressure of supercooled water and ice, this distillation process has not been experimentally realized. In the case of phosphorus, however, where the difference in the vapour pressures is comparatively great, it has been found possible to distil white phosphorus from one part of a closed tube to another, and to there condense it as red phosphorus; and since the vapour pressure of red phosphorus at 350° is less than the vapour pressure of white phosphorus at 200°, it is possible to carry out the distillation from a *colder* part of the tube to a *hotter*, by having white phosphorus at the former and red phosphorus at the latter. Such a process of distillation has been carried out by Troost and Hautefeuille between 324° and 350°.[2]

Relationships similar to those found in the case of phosphorus are also met with in the case of cyanogen and paracyanogen, which have been studied by Chappuis,[1] Troost and Hautefeuille,[2] and Dewar,[3] and also in the case of other organic substances.

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[1] See also Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 177.

[2] *Annales de Chim. et Phys.*, 1874 [5], 2. 154.

Enantiotropy combined with Monotropy.—Not only can polymorphic substances exhibit enantiotropy or monotropy, ut, if the substance is capable of existing in more than two rystalline forms, both relationships may be found, so that me of the forms may be enantiotropic to one another, while e other forms exhibit only monotropy. This behaviour is en in the case of sulphur, which can exist in as many as ht different crystalline varieties. Of these only mononic and rhombic sulphur exhibit the relationship of enantropy, *i.e.* they possess a definite transition point, while other forms are all metastable with respect to rhombic and noclinic sulphur, and remain so up to the melting point; t is to say, they are monotropic modifications.[4]

E. *Liquid Crystals.*

Phenomena observed.—In 1888 it was discovered by initzer[5] that the two substances, cholesteryl acetate and olesteryl benzoate, possess the peculiar property of melting arply at a definite temperature to milky liquids; and that the ter, on being further heated, suddenly become clear, also at definite temperature. Other substances, more especially azoxyanisole and *p*-azoxyphenetole, were, later, found to ssess the same property of having apparently a double elting point.[6] On cooling the clear liquids, the reverse series changes occurred.

The turbid liquids which were thus obtained were found to ossess not only the usual properties of liquids (such as the property of flowing and of assuming a perfectly spherical shape when suspended in a liquid of the same density), but also those properties which had hitherto been observed only in the case of solid crystalline substances, viz. the property of double refraction and of giving interference colours when examined by polarized light; the turbid liquids are *anisotropic*. To such liquids, the optical properties of which were discovered by O. Lehmann, the name *liquid crystals*, or crystalline liquids, was given.

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[1] *Compt. rend.*, 1887, **104**. 1505.

[2] *Compt. rend.*, 1868, **66**. 795.

[3] *Phil. Mag.*, 1884 [5], **18**. 210. See also Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 177.

[4] Brauns, *Jahrbuch für Mineralogie*, 1900, **13**. Beilage-Band, p. 39; Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 181.

[5] *Monatshefte*, 1888, **9**. 435.

[6] Gattermann, *Ber.*, 1890, **23**. 1738.

Nature of Liquid Crystals.—During the past ten years the question as to the nature of liquid crystals has been discussed by a number of investigators, several of whom have contended strongly against the idea of the term "liquid" being applied to the crystalline condition; and various attempts have been made to prove that the turbid liquids are in reality heterogeneous and are to be classed along with emulsions.[2] This view was no doubt largely suggested by the fact that the anisotropic liquids were turbid, whereas the "solid" crystals were clear. Lehmann found, however, that, when examined under the microscope, the "simple" liquid crystals were also clear,[3] the apparent turbidity being due to the aggregation of a number of differently oriented crystals, in the same way as a piece of marble does not appear transparent although composed of transparent crystals.[4]

Further, no proof of the heterogeneity of liquid crystals has yet been obtained, but rather all chemical and physical investigations indicate that they are homogeneous.[5] No separation of a solid substance from the milky, anisotropic liquids has been

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[1] *Zeitschr. physikal. Chem.*, 1889, **4**. 468; *Annalen der Physik*, 1900 [4], **2**. 649.

[2] Quincke, *Annalen der Physik*, 1894 [3], **53**. 613; Tammann, *Annalen der Physik*, 1901 [4], **4**. 524; 1902, **8**. 103; Rotarski, *ibid.*, **4**. 528.

[3] *Annalen der Physik*, 1900 [4], **2**. 649.

[4] *Annalen der Physik*, 1902 [4], **8**. 911.

[5] See, more especially, O. Lehmann, *Annalen der Physik*, 1900 [4], **2**. 649; Reinitzer, *Sitzungsber. kaiserl. Akad. zu Wien.*, 1888, **94**. (2), 719; **97**. (1), 167; Gattermann, *loc. cit.*; Schenck, *Zeitschr. physikal. Chem.*, 1897, **23**. 703; 1898, **25**. 337; **27**. 170; 1899, **28**. 280; Schenck and Schneider, *ibid.*, 1899, **29**. 546; Abegg and Seitz, *ibid.*, 1899, **29**. 491; Hulett, *ibid.*, 1899, **28**. 629.

ted; the anisotropic liquid is in some cases less viscous the isotropic liquid formed at a higher temperature; and emperature of liquefaction is constant, and is affected by ure and admixture with foreign substances exactly as in ase of a pure substance.

quilibrium Relations in the Case of Liquid Crystals.—e, now, we have seen that we are dealing here with sub- es in two crystalline forms (which we may call the solid liquid[1] crystalline form), which possess a definite transi- point, at which transformation of the one form into the r occurs in both directions, we can represent the con-

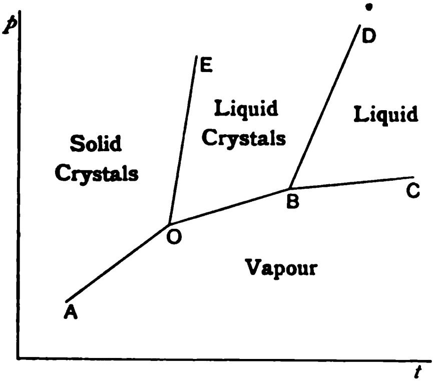

FIG. 12.

ns of equilibrium by a diagram in all respects similar to employed in the case of other enantiotropic substances, sulphur (p. 33).

In Fig. 12 there is given a diagrammatic representation of relationships found in the case of *p*-azoxyanisole.[2]

On account of the fact that all grades of rigidity have been realized en the ordinary solid and the liquid state, in the case both of crys- e and amorphous substances, it has been proposed to abandon the "solid" and "liquid," and to class bodies as "crystalline" or rphous," the passage from the one condition to the other being dis- uous; crystalline bodies possess a certain regular orientation of molecules and a directive force, while in amorphous bodies these are ng (see Lehmann, *Annalen der Physik*, 1900 [4], 2. 696).

Hulett, *loc. cit.*

Although the vapour pressure of the substance in the soli or liquid state, has not been determined, it will be understoo from what we have already learned, that the curves AO, OI BC, representing the vapour pressure of solid crystals, liqui crystals, isotropic liquid, must have the relative positions show in the diagram. Point O, the transition point of the solid int the liquid crystals, lies at 118·27°, and the change of the transition point with the pressure is + 0·032° pro 1 atm. Th transition curve OE slopes, therefore, slightly to the right The point B, the melting point of the liquid crystals, lies a 135·85°, and the melting point is raised 0·0485° pro 1 atm. The curve BD, therefore, also slopes to the right, and more so than the transition curve. In this respect azoxyanisole is different from sulphur.

The areas bounded by the curves represent the conditions for the stable existence of the four single phases, solid crystals, liquid crystals, isotropic liquid and vapour.

The most important substances hitherto found to form liquid crystals are[1] :—

Substance.	Transition point.	Melting point.
Cholesteryl benzoate	145·5°	178·5°
Azoxyanisole	118·3°	135·9°
Azoxyphenetole	134·5°	168·1°
Condensation product from benzaldehyde and benzidine	234°	260°
Azine of *p*-oxyethylbenzaldehyde	172°	196°
Condensation product from *p*-tolylaldehyde and benzidine	231°	—
p-Methoxycinnamic acid	169°	185°

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[1] Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 144.

CHAPTER IV

GENERAL SUMMARY

In the preceding pages we have learned how the principles of the Phase Rule can be applied to the elucidation of various systems consisting of one component. In the present chapter it is proposed to give a short summary of the relationships we have met with, and also to discuss more generally how the Phase Rule applies to other one-component systems. On account of the fact that beginners are sometimes inclined to expect too much of the Phase Rule; to expect, for example, that it will inform them as to the exact behaviour of a substance, it may here be emphasized that the Phase Rule is a general rule; it informs us only as to the general conditions of equilibrium, and leaves the determination of the definite, numerical data to experiment.

Triple Point.—We have already (p. 26) defined a triple point in a one-component system, as being that pressure and temperature at which three phases coexist in equilibrium; it represents, therefore, an invariant system (p. 16). At the triple point also, three curves cut, viz. the curves representing the conditions of equilibrium of the three univariant systems formed by the combination of the three phases in pairs. The most common triple point of a one-component system is, of course, the triple point, solid, liquid, vapour (S–L–V), but other triple points[1] are also possible when, as in the case of sulphur or benzophenone, polymorphic forms occur. Whether or not all the triple points can be experimentally realized will, of course, depend on circumstances. We shall, in the first place, consider only the triple point S–L–V.

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[1] The possible number of triple points in a one-component system is given by the expression $\frac{n(n-1)(n-2)}{1.2.3.}$, where n is the number of phases (Riecke, *Zeitschr. physikal. Chem.*, 1890, **6**. 411). The number of triple points, therefore, increases very rapidly as the number of possible phases increases.

As to the general arrangement of the three univariant curves around the triple point, the following rules may be given. (1) The prolongation of each of the curves beyond the triple point must lie between the other two curves. (2) The middle position at one and the same temperature in the neighbourhood of the triple point is taken by that curve (or its metastable prolongation) which represents the two phases of most widely differing specific volume.[1] That is to say, if a line of constant temperature is drawn immediately above or below the triple point so as to cut the three curves—two stable curves and the metastable prolongation of the third—the position of the curves at that temperature will be such that the middle position is occupied by that curve (or its metastable prolongation) which represents the two phases of most widely differing specific volume.

Now, although these rules admit of a considerable variety of possible arrangements of curves around the triple point,[2] only two of these have been experimentally obtained in the case of the triple point solid—liquid—vapour. At present, therefore, we shall consider only these two cases (Figs. 13 and 14).

An examination of these two figures shows that they satisfy the rules laid down. Each of the curves on being prolonged passes between the other two curves. In the case of substances of the first type (Fig. 13), the specific volume of the solid is greater than that of the liquid (the substance contracts on fusion); the difference of specific volume will, therefore, be greatest between liquid and vapour. The curve, therefore, for liquid and vapour (or its prolongation) must lie between the other two curves; this is seen from the figure to be the case. Similarly, the rule is satisfied by the arrangement of curves in Fig. 14, where the difference of specific volumes is greatest between the solid and vapour. In this case the curve S–V occupies the intermediate position.

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[1] Duhem, *Zeitschr. physikal. Chem.*, 1891, 8. 371. *Cf.* Roozeboom, *Das Heterogene Gleichgewicht*, p. 94 ff.

[2] Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 99.

As we see, the two figures differ from one another only in that the fusion curve OC in one case slopes to the right away from the pressure axis, thus indicating that the melting point is raised by increase of pressure; in the other case, to the left, indicating a lowering of the melting point with the pressure. These conditions are found exemplified in the case of sulphur and ice (pp. 23 and 36). We see further from the two figures, that O in Fig. 13 gives the highest temperature at which the solid can exist, for the curve for solid—liquid slopes back to regions of lower temperature; in Fig. 14, O gives the lowest temperature at which the liquid phase can exist as stable phase.[1]

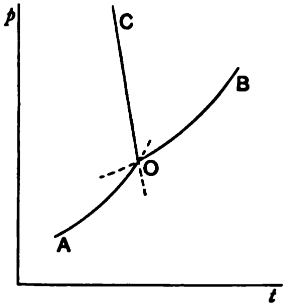

FIG. 13.

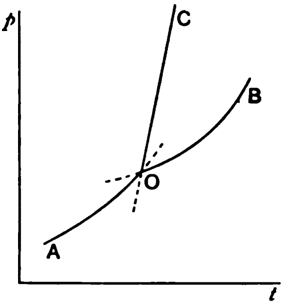

FIG. 14.

Theorems of van't Hoff and of Le Chatelier.—So far we have studied only the conditions under which various systems exist in equilibrium; and we now pass to a consideration of the changes which take place in a system when the externa conditions of temperature and pressure are altered. For all such changes there exist two theorems, based on the laws of thermodynamics, by means of which the alterations in a system can be qualitatively predicted.[2] The first of these, usually known as van't Hoff's *law of movable equilibrium*,[1] states: When the temperature of a system in equilibrium is raised, that reaction takes place which is accompanied by absorption of heat; and, conversely, when the temperature is lowered, that reaction occurs which is accompanied by an evolution of heat.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1888, **2**. 474.

[2] These changes can be predicted *quantitatively*, provided the specific volumes of the phases are known, and the heat effect which accompanies he transformation of one phase into the other.

The second of the two theorems refers to the effect of change of pressure, and states:[2] When the pressure on a system in equilibrium is increased, that reaction takes place which is accompanied by a diminution of volume; and when the pressure is diminished, a reaction ensues which is accompanied by an increase of volume.

The demonstration of the universal applicability of these two theorems is due chiefly to Le Chatelier, who showed that they may be regarded as consequences of the general law of action and reaction. For this reason they are generally regarded as special cases of the more general law, known as the *theorem of Le Chatelier*, which may be stated in the words of Ostwald, as follows:[3] *If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint*, i.e. *one by which its effect is partially annulled.*

This theorem of Le Chatelier is of very great importance, for it applies to all systems and changes of the condition of equilibrium, whether physical or chemical; to vaporization and fusion; to solution and chemical action. In all cases, whenever changes in the external condition of a system in equilibrium are produced, processes also occur within the system which tend to counteract the effect of the external changes.

Changes at the Triple Point.—If now we apply this theorem to equilibria at the triple point S–L–V, and ask what changes will occur in such a system when the external conditions of pressure and temperature are altered, the general answer to the question will be: So long as the three phases are present, no change in the temperature or pressure of the system can occur, but *only changes in the relative amounts of the phases*; that is to say, the effect on the system of change in the external conditions is opposed by the reactions or changes which take place within the system (according to the theorems of van't Hoff and Le Chatelier). We now proceed to discuss what these changes are, and shall consider first the effect of alteration of the temperature at constant volume and constant pressure, and then the effect of alteration of the pressure both when the temperature remains constant and when it varies.

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[1] *Studies on Chemical Dynamics*, translated by Ewan, p. 218.

[2] Le Chatelier, *Compt. rend.*, 1884, 99. 786.

[3] See *Principles of Inorganic Chemistry*, translated by Findlay, p. 130. (Macmillan, 1902.)

When the volume is kept constant, the effect of the addition of heat to a system at the triple point S–L–V differs somewhat according as there is an increase or diminution of volume when the solid passes into the liquid state. In the former and most general case (Fig. 14), addition of heat will cause a certain amount of the solid phase to melt, whereby the heat which is added becomes latent; the temperature of the system therefore does not rise. Since, however, the melting of the solid is accompanied by an increase of volume, whereby an increase of pressure would result, a certain portion of the vapour must condense to liquid, in order that the pressure may remain constant. The total effect of addition of heat, therefore, is to cause both solid and vapour to pass into liquid, *i.e.* there occurs the change S + V → L. It will, therefore, depend on the relative quantities of solid and vapour, which will disappear first. If the solid disappears first, then we shall pass to the system L–V; if vapour disappears first, we shall obtain the system S–L. Withdrawal of heat causes the reverse change, L → S + V; at all temperatures below the triple point the liquid is unstable or metastable (p. 28).

When fusion is accompanied by a diminution of volume (*e.g.* ice, Fig. 13), then, since the melting of the solid phase would decrease the total volume, *i.e.* would lower the pressure, a certain quantity of the solid must also pass into vapour in order that the pressure may be maintained constant. On addition of heat, therefore, there occurs the reaction S → L + V; withdrawal of heat causes the reverse change L + V → S. Above the temperature of the triple point the solid cannot exist; below the triple point both systems, S–L and S–V, can exist, and it will therefore depend on the relative amounts of liquid and vapour which of these two systems is obtained on withdrawing heat from the system at constant volume.

The same changes in the phases occur when heat is added or withdrawn at constant pressure, so long as the three phases are present. Continued addition of heat, however, at constant pressure will ultimately cause the formation of the bivariant system vapour alone; continued withdrawal of heat will ultimately cause the formation of solid alone. This will be readily understood from Fig. 15. The dotted line D′OD is a line of constant pressure; on adding heat, the system passes along the line OD into the region of vapour; on heat being withdrawn, the system passes along OD′ into the area of solid.

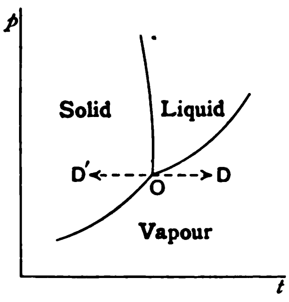

FIG. 15.

Similar changes are produced when the volume of the system is altered. Alteration of volume may take place either while transference of heat to or from the system is cut off (adiabatic change), or while such transference may occur (isothermal change). In the latter case, the temperature of the system will remain constant; in the former case, since at the triple point the pressure must be constant so long as the three phases are present, increase of volume must be compensated by the evaporation of liquid. This, however, would cause the temperature to fall (since communication of heat from the outside is supposed to be cut off), and a portion of the liquid must therefore freeze. In this way the latent heat of evaporation is counterbalanced by the latent heat of fusion. As the result of increase of volume, therefore, the process occurs L → S + V. Diminution of volume, without transference of heat, will bring about the opposite change, S + V → L. In the former case there is ultimately obtained the univariant system S–V; in the latter case there will be d either S–L or L–V according as the vapour or solid lisappears first.

is argument holds good for both types of triple point in Figs. 13 and 14 (p. 55). A glance at these figures ow that increase of volume (diminution of pressure) will ltimately to the system S–V, for at pressures lower than the triple point, the liquid phase cannot exist. Decrease ume (increase of pressure), on the other hand, will lead to the system S–L or L–V, because these systems can t pressures higher than that of the triple point. If the r phase disappears and we pass to the curve S–L, continued ution of volume will be accompanied by a fall in tempera- the case of systems of the first type (Fig. 13), and by a

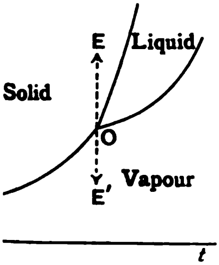

FIG. 16.

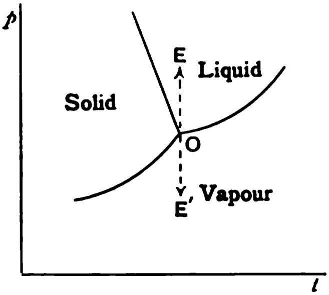

FIG. 17.

temperature in the case of systems of the second type 14).

astly, if the temperature is maintained constant, *i.e.* if heat ass into or out of the system, then on changing the volume ame changes in the phases will take place as described until one of the phases has disappeared. Continued se of volume (decrease of pressure) will then cause the pearance of a second phase, the system passing along the d line OE′ (Figs. 16, 17), so that ultimately there remains the vapour phase. Conversely, diminution of volume ase of pressure) will ultimately lead either to solid 16) or to liquid alone (Fig. 17), the system passing along otted line OE.

In discussing the alterations which may take place at th triple point with change of temperature and pressure, we hav considered only the triple point S–L–V. The same reasoning however, applies, *mutatis mutandis*, to all other triple points, s that if the specific volumes of the phases are known, and th sign of the heat effects which accompany the transformation o one phase into the other, it is possible to predict (by means o the theorem of Le Chatelier) the changes which will be produce in the system by alteration of the pressure and temperature.

In all cases of transformation at the triple point, it shoul be noted that *all three phases are involved in the change*,[1] and no two only; the fact that in the case, say, of the transformatio from solid to liquid, or liquid to solid, at the melting point wit change of temperature, only these two phases appear to b affected, is due to there generally being a large excess of th vapour phase present and to the prior disappearance therefo of the solid or liquid phase.

In the case of triple points at which two solid phases a in equilibrium with liquid, other arrangements of the curve around the triple point are found. It is, however, unnecessar to give a general treatment of these here, since the principle which have been applied to the triple point S–L–V can also b applied to the other triple points.[2]

Triple Point Solid—Solid—Vapour.—The triple poin solid—solid—vapour is one which is of considerable import- ance. Examples of such a triple point have already been given in sulphur and tin, and a list of other substances capable of yielding two solid phases is given below. The triple point S–S–V is not precisely the same as the transition point, but is very nearly so. The transition point is the temperature at which the relative stability of the two solid phases undergoes change, when the vapour phase is absent and the pressure is 1 atm.; whereas at the triple point the pressure is that of the system itself. The transition point, therefore, bears the same relation to the triple point S–S–V as the melting point to the triple point S–L–V.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1888, **2**. 474.

[2] Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 189.

In the following table is given a list of the most important polymorphous substances, and the temperatures of the transition point.[1]

Substance.	Transition temperature.
Ammonium nitrate—	
β-rhombic → α-rhombic	35°
α-rhombic → rhombohedral	83°
Rhombohedral → regular	125°
Mercuric iodide	126°
Potassium nitrate	129°
Silver iodide	145°
Silver nitrate	160°
Sulphur	95·5°
Tetrabrommethane	46·8°
Thallium nitrate—	
Rhombic → rhombohedral	80°
Rhombohedral → regular	142·5°
Thallium picrate	46°
Tin	20°

Sublimation and Vaporization Curves.—We have already seen, in the case of ice and liquid water, that the vapour pressure increases as the temperature rises, the increase of pressure per degree being greater the higher the temperature. The sublimation and vaporization curves, therefore, are not straight lines, but are bent, the convex side of the curve being towards the temperature axis in the ordinary *pt*-diagram.

In the case of sulphur and of tin, we assumed vapour to be given off by the solid substance, although the pressure of the vapour has not hitherto been measured. The assumption, however, is entirely justified, not only on theoretical grounds, but also because the existence of a vapour pressure has been observed in the case of many solid substances at temperatures much below the melting point,[2] and in some cases, *e.g.* camphor,[3] the vapour pressure is considerable.

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[1] Roozeboom, *Das Heterogene Gleichgewicht*, I., p. 125.

[2] Roberts-Austen, *Proc. Roy. Soc.*, **63**. 454 ; Spring, *Zeitschr. physikal. Chem.* 1894, **15**. 65. See also p. 33.

[3] Ramsay and Young, *Phil. Trans.*, 1884, **175**. 461 ; Allen, *Trans. Chem. Soc.*, 1900, **77**. 413.

As the result of a large number of determinations, it has been found that all vapour pressure curves have the same general form alluded to above. Attempts have also been made to obtain a general expression for the quantitative changes in the vapour pressure with change of temperature, but without success. Nevertheless, the *qualitative* changes, or the general direction of the curves, can be predicted by means of the theorem of Le Chatelier.

As we have already learned (p. 16), the Phase Rule takes no account of the molecular complexity of the substances participating in an equilibrium. A dissociating substance, therefore, in contact with its vaporous products of dissociation (*e.g.* ammonium chloride in contact with ammonia and hydrogen chloride), will likewise constitute a univariant system of one component, provided the composition of the vapour phase as a whole is the same as that of the solid or liquid phase (p. 13). For all such substances, therefore, the conditions of equilibrium will be represented by a curve of the same general form as the vapour pressure curve of a non-dissociating substance.[1] The same behaviour is also found in the case of substances which polymerize on passing into the solid or liquid state (*e.g.* red phosphorus). Where such changes in the molecular state occur, however, the time required for equilibrium to be established is, as a rule, greater than when the molecular state is the same in both phases.

From an examination of Figs. 13 and 14, it will be easy to predict the effect of change of pressure and temperature on the univariant systems S–V or L–V. If the volume is kept constant, addition of heat will cause an increase of pressure, the system S–V moving along the curve AO until at the triple point the liquid phase is formed, and the system L–V moving along the curve OB; so long as two phases are present, the condition of the system must be represented by these two curves. Conversely, withdrawal of heat will cause condensation of vapour, and therefore diminution of pressure; the system will therefore move along the vaporization or sublimation curve to lower temperatures and pressures, so long as the system remains univariant.

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[1] Ramsay and Young, *Phil. Trans.* 1886, 177. 87.

If transference of heat to or from the system is prevented, increase of volume (diminution of pressure) will cause the system L–V to pass along the curve BO; liquid will pass into vapour and the temperature will fall. At O solid may appear, and the temperature of the system will then remain constant until the liquid phase has disappeared (p. 58); the system will then follow the curve OA until the solid phase disappears, and we are ultimately left with vapour. On the other hand, diminution of volume (increase of pressure) will cause condensation of vapour, and the system S–V will pass along the curve AO to higher temperatures and pressures; at O the solid will melt, and the system will ultimately pass to the curve OB or to OC (p. 58).

Addition or withdrawal of heat at constant pressure, and increase or diminution of the pressure at constant temperature, will cause the system to pass along lines parallel to the temperature and the pressure axis respectively; the working out of these changes may be left to the reader, guided by what has been said on pp. 58 and 59.

The sublimation curve of all substances, so far as yet found, has its upper limit at the melting point (triple point), although the possibility of the existence of a superheated solid is not excluded. The lower limit is, theoretically at least, at the absolute zero, provided no new phase, *e.g.* a different crystalline modification, is formed. If the sublimation pressure of a substance is greater than the atmospheric pressure at any temperature below the point of fusion, then the substance will *sublime without melting* when heated in an open vessel; and fusion will be possible only at a pressure higher than the atmospheric. This is found, for example, in the case of red phosphorus (p. 45). If, however, the sublimation pressure of a substance at its triple point S–L–V is less than one atmosphere, then the substance will melt when heated in an open vessel.

In the case of the vaporization curve, the upper limit lies at the critical point where the liquid ceases to exist;[1] the lower limit is determined by the range of the metast of the supercooled liquid.

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[1] Tammann has, however, found that the fusion curve (solid in contact with liquid) of phosphonium chloride can be followed up to temperatures above the critical point (*Arch. néer.*, 1901 [2], 6. 244).

The interpolation and extrapolation of vapou curves is rendered very easy by means of a relation Ramsay and Young[1] found to exist between th pressure curves of different substances. It was obs in the case of closely related substances, the ratio solute temperatures corresponding to equal vapour is constant, *i.e.* $\frac{T_1}{T'_1} = \frac{T_2}{T'_2}$. When the two substanc closely related, it was found that the relationship expressed by the equation $\frac{T_1}{T'_1} = \frac{T_2}{T'_2} + c(t' - t)$ wh constant having a small positive or negative value, a are the temperatures at which one of the substanc two values of the vapour pressure in question. B this equation, if the vapour-pressure curve of one s known, the vapour-pressure curve of any other sub be calculated from the values at any two temperat vapour pressure of that substance.

Fusion Curve—Transition Curve.—The fusion c sents the conditions of equilibrium between the liquid phase; it shows the change of the melting substance with change of pressure.

As shown in Figs. 13 and 14, the fusion curve either towards the pressure axis or away from i increase of pressure can either lower or raise the mel It is easy to predict in a qualitative manner the diff of pressure on the melting point in the two cases me we consider the matter in the light of the theorem o elier (p. 56). Water, on passing into ice, expands; if the pressure on the system ice—water be increased will take place which is accompanied by a dim volume, *i.e.* the ice will melt. Consequently, a l perature will be required in order to counteract th increase of pressure; or, in other words, the melting be lowered by pressure. In the second case, the

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[1] *Phil. Mag.*, 1886, **21**. 33.

the liquid to the solid state is accompanied by a diminution of volume; the effect of increase of pressure will therefore be the reverse of that in the previous case.

If the value of the heat of fusion and the alteration of volume accompanying the change of state are known, it is possible to calculate *quantitatively* the effect of pressure.[1]

We have already seen (p. 23) that the effect of pressure on the melting point of a substance was predicted as the result of theoretical considerations, and was first proved experimentally in the case of ice. Soon after, Bunsen[2] showed that the melting point of other substances is also affected by pressure; and in more recent years, ample experimental proof of the change of the melting point with the pressure has been obtained. The change of the melting point is, however, small; as a rule, increase of pressure by 1 atm. changes the melting point by about 0·03°, but in the case of water the change is much less (0·0076°), and in the case of camphor much more (0·13°). In other words, if we take the mean case, an increase of pressure of more than 30 atm. is required to produce a change in the melting point of 1°.

Investigations which were made of the influence of pressure on the melting-point, showed that up to pressures of several hundred atmospheres the fusion curve is a straight line.[3] Tammann[4] has, however, found that on increasing the pressure the fusion curve no longer remains straight, but bends towards the pressure axis, so that, on sufficiently increasing the pressure, a maximum temperature might at length be reached. This maximum has, so far, however, not been attained, although the melting point curves of various substances have been studied up to pressures of 4500 atm. This is to be accounted for partly by the fact that the probable maximum temperature in the case of most substances lies at very great pressures, and also by the fact that other solid phases make their appearance, as, for example, in the case of ice (p. 30).

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[1] See the volume in this series on *Thermodynamics*, by Dr. F. G. Donnan.

[2] *Pogg. Annalen*, 1850, **81**. 562.

[3] Barus, *Amer. Jour. Sci.*, 1892, **42**. 125; Mack, *Compt. rend.*, 1898, **27**. 361; Hulett, *Zeitschr. physikal. Chem.*, 1899, **28**. 629.

[4] *Annalen der Physik*, 1899 [3], **68**. 553, 629; 1900 [4], **1**. 275; **2**. 1; 161. See also Tammann, *Kristallisieren und Schmelzen* (Leipzig, 1903).

As to the upper limit of the fusion curve, the view has been expressed[1] that just as in the case of liquid and vapour, so also in the case of solid and liquid, there exists a critical point at which the solid and the liquid phase become indentical. Experimental evidence, however, does not appear to favour this view.[2]

The *transition point*, like the melting point, is also influenced by the pressure, and in this case also it is found that pressure may either raise or lower the transition point, so that the transition curve may be inclined either away from or towards the pressure axis. The direction of the transition curve can also be predicted if the change of volume accompanying the passage of one form into the other is known. In the case of sulphur, we saw that the transition point is raised by increase of pressure; in the case of the transition of rhombohedral into α-rhombic form of ammonium nitrate, however, the transition point is lowered by pressure, as shown by the following table.[3]

Temperature.	Pressure.
85·85°	1 atm.
84·38°	100 ,,
83·03°	200 ,,
82·29°	250 ,,

So far as investigations have been carried out, it appears that the transition curve is practically a straight line.

Suspended Transformation. Metastable Equilibria.—Hitherto we have considered only systems in stable equilibrium. We have, however, already seen, in the case of water, that on cooling the liquid down to the triple point, solidification did not necessarily take place, although the conditions were such as to allow of its formation. Similarly, we saw that rhombic sulphur can be heated above the transition point, and monoclinic sulphur can be obtained at temperatures below the transition point, although in both cases transformation into a more stable form is possible; the system becomes metastable.

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[1] Ostwald, *Lehrbuch*, II. 2. 373; Poynting, *Phil. Mag.*, 1881 [5], 12. 2; Planck, *Wied. Annalen*, 1882, 15. 446.

[2] Bakhuis Roozeboom, *Das Heterogene Gleichgewicht*, I. p. 91.

[3] Lussana, *Il nuovo Cimento*, 1895 [4], 1. 105.

The same reluctance to form a new phase is observed also in the phenomena of superheating of liquids, and in the "hanging" of mercury in barometers, in which case the vapour phase is not formed. In general, then, we may say that *a new phase will not necessarily be formed immediately the system passes into such a condition that the existence of that phase is possible;* but rather, instead of the system undergoing transformation so as to pass into the most stable condition under the existing pressure and temperature, this transformation will be "suspended" or delayed, and the system will become metastable. Only in the case of the formation of the liquid from the solid phase, in a one-component system, has this reluctance to form a new phase not been observed.

To ensure the formation of the new phase, it is necessary to have that phase present. The presence of the solid phase will prevent the supercooling of the liquid; and the presence of the vapour phase will prevent the superheating of the liquid. However, even in the presence of the more stable phase, transformation of the metastable phase occurs with very varying velocity; in some cases so quickly as to appear almost instantaneous; while in other cases, the change takes place so slowly as to require hundreds of years for its achievement. It is this slow rate of transformation that renders the existence of metastable forms possible, when in contact with the more stable phase. Thus, for example, although calcite is the most stable form of calcium carbonate at the ordinary temperature,[1] the less stable modification, aragonite, nevertheless exists under the ordinary conditions in an apparently very stable state.

As to the amount of the new phase required to bring about the transformation of the metastable phase, quantitative surements have been carried out only in the case of the iation of crystallization in a supercooled liquid.[2] As the result of these investigations, it was found that, in the case of superfused salol, the very small amount of 1×10^{-7} gm. of the solid phase was sufficient to induce crystallization. Crystallization of a supercooled liquid, however, can be initiated only by a "nucleus" of the same substance in the solid state, or, as has also been found, by a nucleus of an isomorphous solid phase; it is not brought about by the presence of any chance solid.

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[1] Foote, *Zeitschr. physikal. Chem.*, 1900, **33**. 740.

[2] Ostwald, *Zeitschr. physikal. Chem.*, 1897, **22**. 289.

Velocity of Transformation.—Attention has already been drawn to the sluggishness with which reciprocal transformation of the polymorphic forms of a substance may occur. In the case of tin, for example, it was found that the white modification, although apparently possessing permanence, is in reality in a metastable state, under the ordinary conditions of temperature and pressure. This great degree of stability is due to the tardiness with which transformation into the grey form occurs.

What was found in the case of tin, is met with also in the case of all transformations in the solid state, but the velocity of the change is less in some cases than in others, and appears to decrease with increase of the valency of the element.[1] To this fact van't Hoff attributes the great permanence of many really unstable (or metastable) carbon compounds.

Reference has been made to the fact that the velocity of transformation can be accelerated by various means. One of the most important of these is the employment of a liquid which has a solvent action on the solid phases. Just as we have seen that at any given temperature the less stable form has the higher vapour pressure, but that at the transition point the vapour pressure of both forms becomes identical, so also it can be proved theoretically, and be shown experimentally, that at a given temperature the solubility of the less stable form is greater than that of the more stable, but that at the transition point the solubility of the two forms becomes identical.[2]

If, then, the two solid phases are brought into contact with a solvent, the less stable phase will dissolve more abundantly than the more stable; the solution will therefore become supersaturated with respect to the latter, which will be deposited. A gradual change of the less stable form, therefore, takes place through the medium of the solvent. In this way the more rapid conversion of white tin into grey in presence of a solution of tin ammonium chloride (p. 40) is to be explained. Although, as a rule, solvents accelerate the transformation of one solid phase into the other, they may also have a retarding influence on the velocity of transformation, as was found by Reinders in the case of mercuric iodide.[1]

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[1] Van't Hoff, *Arch. néer.*, 1901, **6**. 471.

[2] See, for example, the determinations of the solubility of rhombic and monoclinic sulphur, by J. Meyer, *Zeitschr. anorg. Chem.*, 1902, **33**. 140.

The velocity of inversion, also, is variously affected by different solvents, and in some cases, at least, it appears to be slower the more viscous the solvent;[2] indeed, Kastle and Reed state that yellow crystals of mercuric iodide, which, ordinarily, change with considerable velocity into the red modification, have been preserved for more than a year under vaseline.

Temperature, also, has a very considerable influence on the velocity of transformation. The higher the temperature, and the farther it is removed from the equilibrium point (transition point), the greater is the velocity of change. Above the transition point, these two factors act in the same direction, and the velocity of transformation will therefore go on increasing indefinitely the higher the temperature is raised. Below the transition point, however, the two factors act in opposite directions, and the more the temperature is lowered, the more is the effect of removal from the equilibrium point counteracted. A point will therefore be reached at which the velocity is a maximum. Reduction of the temperature below this point causes a rapid falling off in the velocity of change. The point of maximum velocity, however, is not definite, but may be altered by various causes. Thus, Cohen found that in the case of tin, the point of maximum velocity was altered if the metal had already undergone transformation; and also by the presence of different liquids.[3]

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[1] *Zeitschr. physikal. Chem.*, 1899, **32**. 506.

[2] Kastle and Reed, *Amer. Chem. Jour.*, 1902, **27**. 209.

[3] *Zeitschr. physikal. Chem.*, 1900, **35**. 588.

V Lastly, the presence of small quantities of different substances—catalytic agents or catalyzers—has a great influence on the velocity of transformation. Thus, *e.g.*, the conversion of white to red phosphorus is accelerated by the presence of iodine (p. 45).

Greater attention, however, has been paid to the study of the velocity of crystallization of a supercooled liquid, the first experiments in this direction having been made by Gernez[1] on the velocity of crystallization of phosphorus and sulphur. Since that time, the velocity of crystallization of other supercooled liquids has been investigated; such as acetic acid and phenol by Moore;[2] supercooled water by Tumlirz;[3] and a number of organic substances by Tammann,[4] Friedländer and Tammann,[5] and by Bogojawlenski.[6]

In measuring the velocity of crystallization, the supercooled liquids were contained in narrow glass tubes, and the time required for the crystallization to advance along a certain length of the tube was determined, the velocity being expressed in millimetres per minute. The results which have so far been obtained may be summarized as follows. For any given degree of supercooling of a substance, the velocity of crystallization is constant. As the degree of supercooling increases, the velocity of crystallization also increases, until a certain point is reached at which the velocity is a maximum, which has a definite characteristic value for each substance. This maximum velocity remains constant over a certain range of temperature; thereafter, the velocity diminishes fairly rapidly, and, with sufficient supercooling, may become zero. The liquid then passes into a glassy mass, which will remain (practically) permanent even in contact with the crystalline solid.

The velocity of crystallization has also been found to be diminished by the addition of foreign substances, the diminution of the velocity being the same for equimolecular quantities of all substances.[1]

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[1] *Compt. rend.*, 1882, **95.** 1278; 1884, **97.** 1298, 1366, 1433.

[2] *Zeitschr. physikal. Chem.*, 1893, **12.** 545.

[3] *Sitzungsber. Wiener Akad.*, 1894, **103.** II*a*. 226.

[4] *Zeitschr. physikal. Chem.*, **23**-**29.** See also Küster, *ibid.*, **25**–**28.**

[5] *Zeitschr. physikal. Chem.*, 1897, **24.** 152.

[6] *Ibid.*, 1898, **27.** 585.

Law of Successive Reactions.—When sulphur vapour is cooled at the ordinary temperature, it first of all condenses to drops of liquid, which solidify in an amorphous form, and only after some time undergo crystallization; or, when phosphorus vapour is condensed, white phosphorus is first formed, and not the more stable form—red phosphorus. It has also been observed that even at the ordinary temperature (therefore much below the transition point) sulphur may crystallize out from solution in benzene, alcohol, carbon disulphide, and other solvents, in the prismatic form, the less stable prismatic crystals then undergoing transformation into the rhombic form;[2] a similar behaviour has also been observed in the transformation of the monotropic crystalline forms of sulphur.[3]

Many other examples might be given. In organic chemistry, for instance, it is often found that when a substance is thrown out of solution, it is first deposited as a liquid, which passes later into the more stable crystalline form. In analysis, also, rapid precipitation from concentrated solution often causes the separation of a less stable and more soluble amorphous form.

On account of the great frequency with which the prior formation of the less stable form occurs, Ostwald[4] has put forward the *law of successive reactions*, which states that when a system passes from a less stable condition it does not pass directly into the most stable of the possible states; but into the next more stable, and so step by step into the most stable. This law explains the formation of the metastable forms of monotropic substances, which would otherwise not be obtainable. Although it is not always possible to observe the formation of the least stable form, it should be remembered that that may quite conceivably be due to the great velocity of transformation of the less stable into the more stable form. From what we have learned about the velocity of transformation of metastable phases, we can understand that rapid cooling to a low temperature will tend to preserve the less stable form; and, on account of the influence of temperature in increasing the velocity of change, it can be seen that the formation of the less stable form will be more difficult to observe in superheated than in supercooled systems. The factors, however, which affect the readiness with which the less stable modification is produced, appear to be rather various.[1]

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[1] Von Pickardt, *Zeitschr. physikal. Chem.*, 1902, **42**. 17.

[2] Deville, *Compt. rend.*, 1852, **34**. 561; Payen, *ibid.*, 1852, **34**. 508; Debray, *ibid.*, 1858, **46**. 576.

[3] Brauns, *Neues Jahrbuch für Mineralogie*, 1899, **13**. (Beilage Band) 84.

[4] *Lehrbuch*, II. **2**. 445. See also *Principles of Inorganic Chemistry*, p. 207 ff.

Although a number of at least apparent exceptions to Ostwald's law have been found, it may nevertheless be accepted as a very useful generalization which sums up very frequently observed phenomena.

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[1] Schaum and Schönbeck, *Annalen der Physik*, 1902 [4], 8. 652.

CHAPTER V

SYSTEMS OF TWO COMPONENTS—PHENOMENA OF DISSOCIATION

IN the preceding pages we have studied the behaviour of systems consisting of only one component, or systems in which all the phases, whether solid, liquid, or vapour, had the same chemical composition (p. 13). In some cases, as, for example, in the case of phosphorus and sulphur, the component was an elementary substance; in other cases, however, *e.g.* water, the component was a compound. The systems which we now proceed to study are characterized by the fact that the different phases have no longer all the same chemical composition, and cannot, therefore, according to definition, be considered as one-component systems.

In most cases, little or no difficulty will be experienced in deciding as to the *number* of the components, if the rules given on pp. 12 and 13 are borne in mind. If the composition of all the phases, each regarded as a whole, is the same, the system is to be regarded as of the first order, or a one-component system; if the composition of the different phases varies, the system must contain more than one component. If, in order to *express* the composition of all the phases present when the system is in equilibrium, two of the constituents participating in the equilibrium are necessary and sufficient, the system is one of two components. Which two of the possible substances are to be regarded as components will, however, be to a certain extent matter of arbitrary choice.

The principles affecting the choice of components will best learned by a study of the examples to be discussed in the el.

Different Systems of Two Components.—Applying the Phase Rule

$$P + F = C + 2$$

to systems of two components, we see that in order that the system may be invariant, there must be four phases in equilibrium together; two components in three phases constitute a univariant, two components in two phases a bivariant system. In the case of systems of one component, the highest degree of variability found was two (one component in one phase); but, as is evident from the formula, there is a higher degree of freedom possible in the case of two-component systems. Two components existing in only one phase constitute a tervariant system, or a system with three degrees of freedom. In addition to the pressure and temperature, therefore, a third variable factor must be chosen, and as such there is taken the *concentration of the components*. In systems of two components, therefore, not only may there be change of pressure and temperature, as in the case of one-component systems, but the concentration of the components in the different phases may also alter; a variation which did not require to be considered in the case of one-component systems.

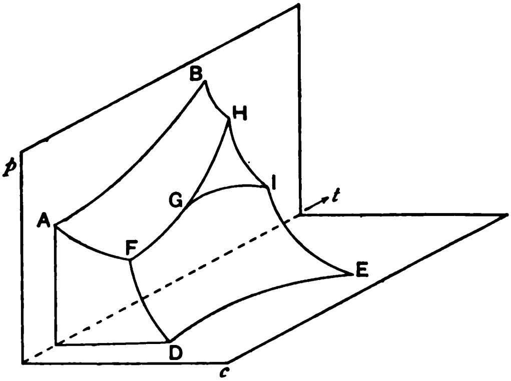

FIG. 18.

Since a two-component system may undergo three possible dependent variations, we should require for the graphic presentation of all the possible conditions of equilibrium a ystem of three co-ordinates in space, three axes being chosen, ay, at right angles to one another, and representing the three ariables—pressure, temperature, and concentration of components (Fig. 18). A curve (*e.g.* AB) in the plane containing the pressure and temperature axes would then represent the change of pressure with the temperature, the concentration remaining unaltered (*pt*-diagram); one in the plane containing the pressure and concentration axes (*e.g.* AF or DF), the change of pressure with the concentration, the temperature remaining constant (*pc*-diagram), while in the plane containing the concentration and the temperature axes, the simultaneous change of these two factors at constant pressure would be represented (*tc*-diagram). If the points on these three curves are joined together, a surface, ABDE, will be formed, and any line on that surface (*e.g.* FG, or GH, or GI) would represent the simultaneous variation of the three factors—pressure, temperature, concentration. Although we shall at a later point make some use of these solid figures, we shall for the present employ the more readily intelligible plane diagram.

The number of different systems which can be formed from two components, as well as the number of the different phenomena which can there be observed, is much greater than in the case of one component. In the case of no two substances, however, have all the possible relationships been studied; so that for the purpose of gaining an insight into the very varied behaviour of two-component systems, a number of different examples will be discussed, each of which will serve to give a picture of some of the relationships.

Although the strict classification of the different systems according to the Phase Rule would be based on the variability of the systems, the study of the many different phenomena, and the correlation of the comparatively large number of different systems, will probably be rendered easiest by grouping these different phenomena into classes, each of these classes being studied with the help of one or more typical examples. The order of treatment adopted here is, of course, quite arbitrary;

but has been selected from considerations of simplicity and clearness.

PHENOMENA OF DISSOCIATION.

Bivariant Systems.—As the first examples of the equilibria between a substance and its products of dissociation, we shall consider very briefly those cases in which there is one solid phase in equilibrium with vapour. Reference has already been made to such systems in the case of ammonium chloride. On being heated, ammonium chloride dissociates into ammonia and hydrogen chloride. Since, however, in that case the vapour phase has the same total composition as the solid phase, viz. $NH_3 + HCl = NH_4Cl$, the system consists of only one component existing in two phases; it is therefore univariant, and to each temperature there will correspond a definite vapour pressure (dissociation pressure).[1]

If, however, excess of one of the products of dissociation be added, the system becomes one of two components.

In the first place, analysis of each of the two phases yields as the composition of each, solid: $NH_3 + HCl$; vapour: $mNH_3 + nHCl$. Obviously the smallest number of substances by which the composition of the two phases can be expressed is two; that is, the number of components is two. What, then, are the components? The choice lies between $NH_3 + HCl$, $NH_4Cl + NH_3$, and $NH_4Cl + HCl$; for the three substances, ammonium chloride, ammonia, hydrogen chloride, are the only ones taking part in the equilibrium of the system.

Of these three pairs of components, we should obviously choose as the most simple NH_3 and HCl, for we can then represent the composition of the two phases as the *sum* of the two components. If one of the other two possible pairs of components be chosen, we should have to introduce negative quantities of one of the components, in order to represent the composition of the vapour phase. Although it must be allowed that the introduction of negative quantities of a component in such cases is quite permissible, still it will be tter to adopt the simpler and more direct choice, whereby e composition of each of the phases is represented as a sum two components in varying proportions (p. 12).

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[1] Ramsay and Young, *Phil. Trans.*, 1886, 177. 87.

If, therefore, we have a solid substance, such as ammonium hloride, which dissociates on volatilization, and if the products f dissociation are added in varying amounts to the system, we hall have, in the sense of the Phase Rule, a *two-component ystem existing in two phases.* Such a system will possess two degrees of freedom. At any given temperature, not only the pressure, but also the composition, of the vapour-phase, *i.e.* the concentration of the components, can vary. Only after one of these independent variables, pressure or composition, has been arbitrarily fixed does the system become univariant, and exhibit a definite, constant pressure at a given temperature.

Now, although the Phase Rule informs us that at a given temperature change of composition of the vapour phase will be accompanied by change of pressure, it does not cast any light on the relation between these two variables. This relationship, however, can be calculated theoretically by means of the Law of Mass Action.[1] From this we learn that in the case of a substance which dissociates into equivalent quantities of two gases, the product of the partial pressures of the gases is constant at a given temperature.

This has been proved experimentally in the case of ammonium hydrosulphide, ammonium cyanide, phosphonium bromide, and other substances.[2]

Univariant Systems.—In order that a system of two components shall possess only one degree of freedom, three phases must be present. Of such systems, there are seven possible, viz. S–S–S, S–S–L, S–S–V, L–L–L, S–L–L, L–L–V, S–L–V; S denoting solid, L liquid, and V vapour. In the present chapter we shall consider only the systems S–S–V, *i.e.* those systems in which there are two solid phases and a vapour phase present.

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[1] See volume in this series on *Chemical Dynamics*, by Dr. J. W. Mellor.

[2] Isambert, *Compt. rend.*, 1881, **92.** 919; 1882, **94.** 958; 1883, **96.** 643. Walker and Lumsden, *Jour. Chem. Soc.*, 1897, **71.** 428.

As an example of this, we may first consider the wel case of the dissociation of calcium carbonate. This su on being heated dissociates into calcium oxide, or qui and carbon dioxide, as shown by the equation $CaCO_3$ + CO_2. In accordance with our definition (p. 9), w here two solid phases, the carbonate and the quick-li one vapour phase; the system is therefore univaria each temperature, therefore, there will correspond a definite maximum pressure of carbon dioxide (diss pressure), and this will follow the same law as the pressure of a pure liquid (p. 19). More particularly, be independent of the relative or absolute amounts of solid phases, and of the volume of the vapour phase. temperature is maintained constant, increase of volu cause the dissociation of a further amount of the ca until the pressure again reaches its maximum value sponding to the given temperature. Diminution of vol the other hand, will bring about the combination of a quantity of the carbon dioxide with the calcium oxide u pressure again reaches its original value.

The dissociation pressure of calcium carbonate w studied by Debray,[1] but more exact measurements hav made by Le Chatelier,[2] who found the following corresp values of temperature and pressure:—

Temperature.	Pressure in cm. mercury.
547°	2·7
610°	4·6
625°	5·6
740°	25·5
745°	28·9
810°	67·8
812°	76·3
865°	133·3

From this table we see that it is only at a temp of about 812° that the pressure of the carbon becomes equal to atmospheric pressure. In a vessel o e air, therefore, the complete decomposition of the calcium rbonate would not take place below this temperature by the ere heating of the carbonate. If, however, the carbon ioxide is removed as quickly as it is formed, say by a current f air, then the entire decomposition can be made to take place t a much lower temperature. For the dissociation equilibrium f the carbonate depends only on the partial pressure of the carbon dioxide, and if this is kept small, then the decomposition can proceed, even at a temperature below that at which the pressure of the carbon dioxide is less than atmospheric pressure.

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[1] *Compt. rend.*, 1867, 64. 603.

[2] *Compt. rend.*, 1883, 102.

Ammonia Compounds of Metal Chlorides.—Ammonia possesses the property of combining with various substances, chiefly the halides of metals, to form compounds which again yield up the ammonia on being heated. Thus, for example, on passing ammonia over silver chloride, absorption of the gas takes place with formation of the substances $AgCl,3NH_3$ and $2AgCl,3NH_3$, according to the conditions of the experiment. These were the first known substances belonging to this class, and were employed by Faraday in his experiments on the liquefaction of ammonia. Similar compounds have also been obtained by the action of ammonia on silver bromide, iodide, cyanide, and nitrate; and with the halogen compounds of calcium, zinc, and magnesium, as well as with other salts. The behaviour of the ammonia compounds of silver chloride is typical for the compounds of this class, and may be briefly considered here.

It was found by Isambert[1] that at temperatures below 15°, silver chloride combined with ammonia to form the compound $AgCl,3NH_3$, while at temperatures above 20° the compound $2AgCl,3NH_3$ was produced. On heating these substances, ammonia was evolved, and the pressure of this gas was found in the case of both compounds to be constant at a given temperature, but was greater in the case of the former than in the case of the latter substance; the pressure, further, was independent of the amount decomposed. The behaviour of these two substances is, therefore, exactly analogous to that shown by calcium carbonate, and the explanation is also similar.

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[1] *Compt. rend.*, 1868, **66**. 1259.

Regarded from the point of view of the Phase Rule, we se that we are here dealing with two components, AgCl and NH. On being heated, the compounds decompose according to the equations :—

$$2(AgCl,3NH_3) \rightleftarrows 2AgCl,3NH_3 + 3NH_3.$$
$$2AgCl,3NH_3 \rightleftarrows 2AgCl + 3NH_3.$$

There are, therefore, three phases, viz. $AgCl,3NH_3$; $2AgCl,3NH_3$, and NH_3, in the one case; and $2AgCl,3NH_3$; AgCl and NH_3 in the other. These two systems are therefore univariant, and to each temperature there must correspond a definite pressure of dissociation, quite irrespective of the amounts of the phases present. Similarly, if, at constant temperature, the volume is increased (or if the ammonia which is evolved is pumped off), the pressure will remain constant so long as two solid phases, $AgCl,3NH_3$ and $2AgCl,3NH_3$, are present, *i.e.* until the compound richer in ammonia is completely decomposed, when there will be a sudden fall in the pressure to the value corresponding to the system $2AgCl,3NH_3$—AgCl—NH_3. The pressure will again remain constant at constant temperature, until all the ammonia has been pumped off, when there will again be a sudden fall in the pressure to that of the system formed by solid silver chloride in contact with its vapour.

The reverse changes take place when the pressure of the ammonia is gradually increased. If the volume is continuously diminished, the pressure will first increase until it has reached a certain value; the compound $2AgCl,3NH_3$ can then be formed, and the pressure will now remain constant until all the silver chloride has disappeared. The pressure will again rise, until it has reached the value at which the compound $AgCl,3NH_3$ can be formed, when it will again remain constant until the complete disappearance of the lower compound. *There is no gradual change of pressure* on passing from one system to another; but the changes are abrupt, as is demanded by the Phase Rule, and as experiment has conclusively proved.[1]

The dissociation pressures of the two compounds of silve de and ammonia, as determined by Isambert,[1] are given following table:—

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[1] Horstmann, *Ber.*, 1876, 9. 749.

$AgCl,3NH_3$.		$2AgCl,3NH_3$.	
Temperature.	Pressure.	Temperature.	Pressure.
0°	29·3 cm.	20·0°	9·3 cm.
10·6°	50·5 ,,	31·0°	12·5 ,,
17·5°	65·5 ,,	47·0°	26·8 ,,
24·0°	93·7 ,,	58·5°	52·8 ,,
28·0°	135·5 ,,	69·0°	78·6 ,,
34·2°	171·3 ,,	71·5°	94·6 ,,
48·5°	241·4 ,,	77·5°	119·8 ,,
51·5°	413·2 ,,	83·5°	159·3 ,,
54·0°	464·1 ,,	86·1°	181·3 ,,
		88·5°	201·3 ,,

he conditions for the formation of these two compounds, assing ammonia over silver chloride, to which reference already been made, will be readily understood from the e tables. In the case of the triammonia mono-chloride, dissociation pressure becomes equal to atmospheric pres- at a temperature of about 20°; above this temperature, efore, it cannot be formed by the action of ammonia at ospheric pressure on silver chloride. The triammonia loride can, however, be formed, for its dissociation pressure is temperature amounts to only 9 cm., and becomes equal he atmospheric pressure only at a temperature of about 68°; this temperature, therefore, constitutes the limit above ch no combination can take place between silver chloride ammonia under atmospheric pressure.

Attention may be here drawn to the fact, to which reference also be made later, that *two* solid phases are necessary in er that the dissociation pressure at a given temperature shall efinite; *and for the exact definition of this pressure it is neces- to know, not merely what is the substance undergoing disso- ion, but also what is the solid product of dissociation formed.* the definition of the equilibrium, the latter is as important he former. We shall presently find proof of this in the case of an analogous class of phenomena, viz. the dissociation of hydrates.

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[1] *Loc. cit.*

Salts with Water of Crystallization.—In the case of th dehydration of crystalline salts containing water of crystalli tion, we meet with phenomena which are in all respects simil to those just studied. A salt hydrate on being heated di sociates into a lower hydrate (or anhydrous salt) and wat vapour. Since we are dealing with two components—salt a water[1]—in three phases, viz. hydrate *a*, hydrate *b* (or anhy drous salt), and vapour, the system is univariant, and to eac temperature there will correspond a certain, definite vapou pressure (the dissociation pres sure), which will be indepe dent of the relative or absolut amounts of the phases, *i.e.* o the amount of hydrate whic has already undergone diss ciation or dehydration.

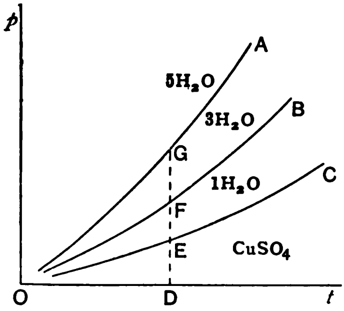

FIG. 19.

The constancy of the dis sociation pressure had bee proved experimentally by several investigators[2] a num ber of years before the theo retical basis for its necessity had been given. In the case of salts capable of forming more than one hydrate, we should obtain a series of dissociation curves (*pt*-curves), as in the case of the different hydrates of copper sulphate. In Fig. 19 there are represented diagrammatically the vapour-pressure curves of the following univariant systems of copper sulphate and water:—

$$\text{Curve OA}: \quad CuSO_4,5H_2O \rightleftarrows CuSO_4,3H_2O + 2H_2O.$$
$$\text{Curve OB}: \quad CuSO_4,3H_2O \rightleftarrows CuSO_4,H_2O + 2H_2O.$$
$$\text{Curve OC}: \quad CuSO_4,H_2O \rightleftarrows CuSO_4 + H_2O.$$

Let us now follow the changes which take place o creasing the pressure of the aqueous vapour in contact with hydrous copper sulphate, the temperature being meanwhile aintained constant. If, starting from the point D, we slowly dd water vapour to the system, the pressure will gradually rise, ithout formation of hydrate taking place; for at pressures elow the curve OC only the anhydrous salt can exist. At E, owever, the hydrate $CuSO_4,H_2O$ will be formed, and as there re now three phases present, viz. $CuSO_4$, $CuSO_4,H_2O$, and apour, the system becomes *univariant;* and since the temperaure is constant, the pressure must also be constant. Continued addition of vapour will result merely in an increase in the amount of the hydrate, and a decrease in the amount of the anhydrous salt. When the latter has entirely disappeared, *i.e.* has passed into hydrated salt, the system again becomes *bivariant*, and passes along the line EF; the pressure gradually increases, therefore, until at F the hydrate $3H_2O$ is formed, and the system again becomes univariant; the three phases present are $CuSO_4,H_2O$, $CuSO_4,3H_3O$, vapour. The pressure will remain constant, therefore, until the hydrate $1H_2O$ has disappeared, when it will again increase till G is reached; here the hydrate $5H_2O$ is formed, and the pressure once more remains constant until the complete disappearance of the hydrate $3H_2O$ has taken place.

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[1] For the reasons for choosing anhydrous salt and water instead of salt hydrate and water as components, see p. 14.

[2] See Ostwald, *Lehrbuch*, II. 2. 527.

Conversely, on dehydrating $CuSO_4,5H_2O$ at constant temperature, we should find that the pressure would maintain the value corresponding to the dissociation pressure of the system $CuSO_4,5H_2O$—$CuSO_4,3H_2O$—vapour, until all the hydrate $5H_2O$ had disappeared; further removal of water would then cause the pressure to fall *abruptly* to the pressure of the system $CuSO_4,3H_2O$—$CuSO_4,H_2O$—vapour, at which value it would again remain constant until the tri-hydrate had passed into the monohydrate, when a further sudden diminution of the pressure would occur. This behaviour is represented diagrammatically in Fig. 20, the values of the pressure being hose at 50°.

Efflorescence.—From Fig. 19 we are enabled to predict the onditions under which a given hydrated salt will effloresce hen exposed to the air. We have just learned that copper sulphate pentahydrate, for example, will not be formed unle the pressure of the aqueous vapour reaches a certain valu and that conversely, if th vapour pressure falls belo the dissociation pressure the pentahydrate, this will undergo dehydratio From this, then, it is ev dent that a crystalline hydrate will effloresce wh exposed to the air, if th partial pressure of the wat vapour in the air is low than the dissociation pre sure of the hydrate. the ordinary temperature the dissociation pressure of copp sulphate is less than the pressure of water vapour in the ai and therefore copper sulphate does not effloresce. In the ca of sodium sulphate decahydrate, however, the dissociatio pressure is greater than the normal vapour pressure in a room, and this salt therefore effloresces.

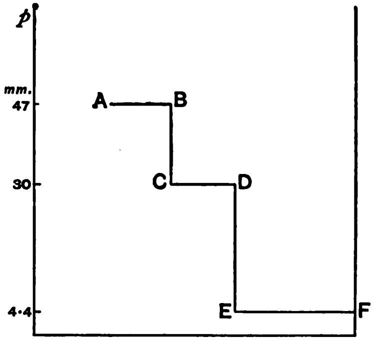

FIG. 20.

Indefiniteness of the Vapour Pressure of a Hydrat.— Reference has already been made (p. 81), in the case of the ammonia compounds of the metal chlorides, to the importance of the solid product of dissociation for the definition of the dissociation pressure. Similarly also in the case of a hydrated salt. A salt hydrate in contact with vapour constitutes only a bivariant system, and can exist therefore at different values of temperature and pressure of vapour, as is seen from the diagram, Fig. 19. Anhydrous copper sulphate can exist in contact with water vapour at all values of temperature and pressure lying in the field below the curve OC; and the hydrate $CuSO_4,H_2O$ can exist in contact with vapour at all values of temperature and pressure in the field BOC. Similarly, each of the other hydrates can exist in contact with vapour at different values of temperature and pressure.

From the Phase Rule, however, we learn that, in order that at a given temperature the pressure of a two-component system ay be constant, there must be three phases present. Strictly, erefore, we can speak only of the vapour pressure of a *system;* nd since, in the cases under discussion, the hydrates dissociate nto a solid and a vapour, any statement as to the vapour ressure of a hydrate has a definite meaning *only when the econd solid phase produced by the dissociation is given.* The everyday custom of speaking of the vapour pressure of a hydrated salt acquires a meaning only through the assumption, tacitly made, that the second solid phase, or the solid produced by the dehydration of the hydrate, is the *next lower* hydrate, where more hydrates than one exist. That a hydrate always dissociates in such a way that the next lower hydrate is formed is, however, by no means certain; indeed, cases have been met with where apparently the anhydrous salt, and not the lower hydrate (the existence of which was possible), was produced by the dissociation of the higher hydrate.[1]

That a salt hydrate can exhibit different vapour pressures according to the solid product of dissociation, can not only be proved theoretically, but it has also been shown experimentally to be a fact. Thus $CaCl_2,6H_2O$ can dissociate into water vapour and either of two lower hydrates, each containing four molecules of water of crystallization, and designated respectively as $CaCl_2,4H_2O\alpha$, and $CaCl_2,4H_2O\beta$. Roozeboom [2] has shown that the vapour pressure which is obtained differs according to which of these two hydrates is formed, as can be seen from the following figures:—

Temperature.	Pressure of System.	
	$CaCl_2,6H_2O$; $CaCl_2,4H_2O\alpha$; vapour.	$CaCl_2,6H_2O$; $CaCl_2,4H_2O\beta$; vapour.
− 15°	0·027 cm.	0·022 cm.
0	0·092 „	0·076 „
+ 10	0·192 „	0·162 „
20	0·378 „	0·315 „
25	0·508 „	0·432 „
29·2	—	0·567 „
29·8	0·680 „	—

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[1] Ostwald, *Lehrbuch*, II. 2. 538.

[2] *Zeitschr. physikal. Chem.*, 1889, 4. 43.

By reason of the non-recognition of the importance of the solid dissociation product for the definition of the dissociation pressure of a salt hydrate, many of the older determinations lose much of their value.

Suspended Transformation.—Just as in systems of one component we found that a new phase was not necessarily formed when the conditions for its existence were established, so also we find that even when the vapour pressure is lowered below the dissociation pressure of a system, dissociation does not necessarily occur. This is well known in the case of Glauber's salt, first observed by Faraday. Undamaged crystals of $Na_2SO_4,10H_2O$ could be kept unchanged in the open air, although the vapour pressure of the system $Na_2SO_4,10H_2O$—Na_2SO_4—vapour is greater than the ordinary pressure of aqueous vapour in the air. That is to say, the possibility of the formation of the new phase Na_2SO_4 was given; nevertheless this new phase did not appear, and the system therefore became metastable, or unstable with respect to the anhydrous salt. When, however, a trace of the new phase—the anhydrous salt—was brought in contact with the hydrate, transformation occurred; the hydrate effloresced.

The possibility of suspended transformation or the non-formation of the new phases must also be granted in the case where the vapour pressure is raised above that corresponding to the system hydrate—anhydrous salt (or lower hydrate)—vapour; in this case the formation of the higher hydrate becomes a possibility, but not a certainty. Although there is no example of this known in the case of hydrated salts, the suspension of the transformation has been observed in the case of the compounds of ammonia with the metal chlorides (p. 79). Horstmann,[1] for example, found that the pressure of ammonia in contact with $2AgCl,3NH_3$ could be raised to a value higher than the dissociation pressure of $AgCl,3NH_3$ without this compound being formed. We see, therefore, that even when the existence of the higher compound in contact with the lower became possible, the higher compound was not immediately formed.

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[1] *Ber.*, 1876, 9. 749.

Range of Existence of Hydrates.—In Fig. 19 the vapour ressure curves of the different hydrates of copper sulphate are epresented as maintaining their relative positions throughout he whole range of temperatures. But this is not necessarily he case. It is possible that at some temperature the vapour pressure curve of a lower hydrate may cut that of a higher hydrate. At temperatures above the point of intersection, the lower hydrate would have a higher vapour pressure than the higher hydrate, and would therefore be metastable with respect to the latter. The range of stable existence of the lower hydrate would therefore end at the point of intersection. This appears to be the case with the two hydrates of sodium sulphate, to which reference will be made later.[1]

Constancy of Vapour Pressure and the Formation of Compounds.—We have seen in the case of the salt hydrates that the continued addition of the vapour phase to the system caused an increase in the pressure until at a definite value of the pressure a hydrate is formed; the pressure then becomes constant, and remains so, until one of the solid phases has disappeared. Conversely, on withdrawing the vapour phase, the pressure remained constant so long as any of the dissociating compound was present, independently of the degree of the decomposition (p. 83). This behaviour, now, has been employed for the purpose of determining whether or not definite chemical compounds are formed. Should compounds be formed between the vapour phase and the solid, then, on continued addition or withdrawal of the vapour phase, it will be found that the vapour pressure remains constant for a certain time, and will then suddenly assume a new value, at which it will again remain constant. By this method, Ramsay [2] found that no definite hydrates were formed in the case of ferric and aluminium oxides, but that two are formed in the case of lead oxide, viz. $2PbO,H_2O$ and $3PbO,H_2O$.

The method has also been applied to the investigation of the so-called palladium hydride,[3] and the results obtained appear to show that no compound is formed. Reference will, however, be made to this case later (Chap. X.).

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[1] See, for example, van't Hoff, *Lectures on Theoretical and Physical Chemistry*, I. p. 62 (Arnold).

[2] *Jour. Chem. Soc.*, 1877, **32**. 395.

[3] Hoitsema, *Zeitschr. physikal. Chem.*, 1895, **17**. 1.

Measurement of the Vapour Pressure of Hydrates.—For the purpose of measuring the small pressures exerted by the vapour of salt hydrates, use is very generally made of a differential manometer called the *Bremer-Frowein tensimeter.*[1]

This apparatus has the form shown in Fig. 21. It consists of a U-tube, the limbs of which are bent close together, and placed in front of a millimetre scale. The bend of the tube is filled with oil or other suitable liquid, *e.g.* bromonaphthalene. If it is desired to measure the dissociation pressure of, say, a salt hydrate, concentrated sulphuric acid is placed in the flask *e*, and a quantity of the hydrate, well dried and powdered,[2] in the bulb *d*. The necks of the bulbs *d* and *e* are then sealed off. Since, as we have learned, suspended transformation may occur, it is advisable to first partially dehydrate the salt, in order to ensure the presence of the second solid product of dissociation; the value of the dissociation pressure being independent of the degree of dissociation of the hydrate (p. 83). The small bulbs *d* and *e* having been filled, the apparatus is placed on its side, so as to allow the liquid to run from the bend of the tube into the bulbs *a* and *b*; it is then exhausted through *f* by means of a mercury pump, and sealed off. The apparatus is now placed in a perpendicular position in a thermostat, and kept at constant temperature until equilibrium is established. Since the vapour pressure on the side containing the sulphuric acid may be regarded as zero, the difference in level of the

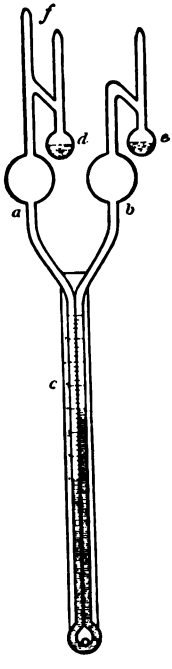

FIG. 21.

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[1] *Zeitschr. physikal. Chem.*, 1887, **1.** 5; 1895, **17.** 52.

[2] It is important to powder the salt, since otherwise the dehydration of the hydrate and the production of equilibrium occurs with comparatively great tardiness.

surfaces of liquid in the U-tube gives directly the dis-
ation pressure of the hydrate in terms of the particular
id employed; if the density of the latter is known, the
ssure can then be calculated to cm. of mercury.

CHAPTER VI

SOLUTIONS

Definition.—In all the cases which have been considered in the preceding pages, the different phases—with the exception of the vapour phase—consisted of a single substance of definite composition, or were definite chemical individuals.[1] But this invariability of the composition is by no means imposed by the Phase Rule; on the contrary, we shall find in the examples which we now proceed to study, that the participation of phases of variable composition in the equilibrium of a system is in no way excluded. To such phases of variable composition there is applied the term *solution.* A solution, therefore, is to be defined as *a homogeneous mixture, the composition of which can undergo continuous variation within certain limits;* the limits, namely, of its existence.[2]

From this definition we see that the term solution is not restricted to any particular physical state of substances, but includes within its range not only the liquid, but also the gaseous and solid states. We may therefore have solutions of gases in liquids, and of gases in solids; of liquids in liquids or in solids; of solids in liquids, or of solids in solids. Solutions of gases in gases are, of course, also possible; since, however, gas solutions never give rise to more than one phase, their ıt does not come within the scope of the Phase Rule, eals with heterogeneous equilibria.

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[1] A chemical individual is a substance which persists as a phase of constant composition when the conditions of temperature, pressure, and composition of the other phases present, undergo continuous alteration within certain limits—the limits of existence of the substance (Wald, *Zeitschr. physikal. Chem.*, 1897, **24.** 648).

[2] Van't Hoff, *Zeitschr. physikal. Chem.*, 1890, **5.** 323; Ostwald, *Lehrbuch*, I. 606.

ıould also be emphasized that the definition of solution bove, neither creates nor recognizes any distinction solvent and dissolved substance (solute); and, indeed, ersistent use of these terms and the attempt to per- y label the one or other of two components as the or the solute, can only obscure the true relationships ravate the difficulty of their interpretation. In all cases d be remembered that we are dealing with equilibria . two components (we confine our attention in the first to such), the solution being constituted of these com- in variable and varying amounts. The change from where the one component is in great excess (ordinarily ıe solvent) to that in which the other component pre- :es, may be quite gradual, so that it is difficult or ble to say at what point the one component ceases to olvent and becomes the solute. The adoption of this int need not, however, preclude one from employing ventional terms solvent and solute in ordinary language, ly when reference is made only to some particular con- f equilibrium of the system, when the concentration of components in the solution is widely different.

SOLUTIONS OF GASES IN LIQUIDS.

the first class of solutions to which we shall turn our n, there may be chosen the solutions of gases in liquids, quilibria between a liquid and a gas. These equilibria onstitute a part of the equilibria to be studied more Chapter VIII.; but since the two-phase systems formed olutions of gases in liquids are among the best-known two-component systems, a short section may be here to their treatment.

:n a gas is passed into a liquid, absorption takes place eater or less extent, and a point is at length reached ıe liquid absorbs no more of the gas; a condition of ium is attained, and the liquid is said to be saturated with the gas. In the light of the Phase Rule, now, such system is bivariant (two components in two phases); and tw of the variable factors, pressure, temperature, and concentratio of the components, must therefore be chosen in order that th condition of the system may be defined. If the concentratio and the temperature are fixed, then the pressure is also defined or under given conditions of temperature and pressure, the concentration of the gas in the solution must have a definite value. If, however, the temperature alone is fixed, the concentration and the pressure can alter; a fact so well known that it does not require to be further insisted on.

As to the way in which the solubility of a gas in a liquid varies with the pressure, the Phase Rule of course does not state; but guidance on this point is again yielded by the theorem of van't Hoff and Le Chatelier. Since the absorption of a gas is in all cases accompanied by a diminution of the total volume, this process must take place with increase of pressure. This, indeed, is stated in a quantitative manner in the law of Henry, according to which the amount of a gas absorbed is proportional to the pressure. But this law must be modified in the case of gases which are very readily absorbed; the *direction of change* of concentration with the pressure will, however, still be in accordance with the theorem of Le Chatelier.

If, on the other hand, the pressure is fixed, then the concentration will vary with the temperature; and since the absorption of gases is in all cases accompanied by the evolution of heat, the solubility is found, in accordance with the theorem of Le Chatelier, to diminish with rise of temperature.

In considering the changes of pressure accompanyin changes of concentration and temperature, a distinction mus be drawn between the total pressure and the partial pressure o the dissolved gas, in cases where the solvent is volatile. I these cases, the law of Henry applies not to the total pressu of the vapour, but only to the partial pressure of the dissolve gas.

SOLUTIONS OF LIQUIDS IN LIQUIDS.

When mercury and water are brought together, the two liquids remain side by side without mixing. Strictly speaking, mercury undoubtedly dissolves to a certain extent in the water, and water no doubt dissolves, although to a less extent, in the mercury; the amount of substance passing into solution is, however, so minute, that it may, for all practical purposes, be left out of account, so long as the temperature does not rise much above the ordinary.[1] On the other hand, if alcohol and water be brought together, complete miscibility takes place, and one homogeneous solution is obtained. Whether water be added in increasing quantities to pure alcohol, or pure alcohol be added in increasing amount to water, at no point, at no degree of concentration, is a system obtained containing more than one liquid phase. At the ordinary temperature, water and alcohol can form only two phases, liquid and vapour. If, however, water be added to ether, or if ether be added to water, solution will not occur to an indefinite extent; but a point will be reached when the water or the ether will no longer dissolve more of the other component, and a further addition of water on the one hand, or ether on the other, will cause the formation of two liquid layers, one containing excess of water, the other excess of ether. We shall, therefore, expect to find all grades of miscibility, from almost perfect immiscibility to perfect miscibility, or miscibility in all proportions. In cases of perfect immiscibility, the components do not affect one another, and the system therefore remains unchanged. Such cases do not call for treatment here. We have to concern ourselves here only with the second and third cases, viz. with cases of complete and of partial miscibility. There is no essential difference between the two classes, for, as we shall see, the one passes into the other with change of temperature. The formal separation into two groups is based on the miscibility relations at ordinary temperatures.

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[1] That mercury does dissolve in water can be argued from analogy, say, with mercury and bromonaphthalene. At the ordinary temperature these two liquids appear to be quite insoluble in one another, but at a temperature of 380° the mercury dissolves in appreciable quantity; for on heating a tube containing bromonaphthalene over mercury the latter sublimes *through* the liquid bromonaphthalene and condenses on the upper surface of the tube.

Partial or Limited Miscibility.—In accordance with the Phase Rule, a pure liquid in contact with its vapour constitutes a univariant system. If, however, a small quantity of a second substance is added, which is capable of dissolving in the first, a bivariant system will be obtained; for there are now two components and, as before, only two phases—the homogeneous liquid solution and the vapour. At constant temperature, therefore, both the composition of the solution and the pressure of the vapour can undergo change; or, if the composition of the solution remains unchanged, the pressure and the temperature can alter. If the second (liquid) component is added in increasing amount, the liquid will at first remain homogeneous, and its composition and pressure will undergo a continuous change; when, however, the concentration has reached a definite value, solution no longer takes place; two liquid phases are produced. Since there are now three phases present, two liquids and vapour, the system is univariant; at a given temperature, therefore, the concentration of the components in the two liquid phases, as well as the vapour pressure, must have definite values. Addition of one of the components, therefore, cannot alter the concentrations or the pressure, but can only cause a change in the relative amounts of the phases.

The two liquid phases can be regarded, the one as a solution of the component I. in component II., the other as a solution of component II. in component I. If the pressure is maintained constant, then to each temperature there will correspond a definite concentration of the components in the two liquid phases; and addition of excess of one will merely alter the relative amounts of the two solutions. As the temperature changes, the composition of the two solutions will change, and there will therefore be obtained two solubility curves, one showing the solubility of component I. in component II., the other showing the solubility of component II. in component I. Since heat may be either evolved or absorbed when one liquid dissolves in another, the solubility may diminish or increase se of temperature. The two solutions which at a given :ature correspond to one another are known as *conjugate* *rs.*

e solubility relations of partially miscible liquids have tudied by Guthrie,[1] and more especially by Alexejeff[2] y Rothmund.[3] A considerable variety of curves have btained, and we shall therefore discuss only a few of the it cases which may be taken as typical of the rest.

enol and Water.—When phenol is added to water at the y temperature, solution takes place, and a homogeneous is produced. When, however, the concentration of the in the solution has risen to about 8 per cent., phenol to be dissolved; and a further addition of it causes the ion of a second liquid phase, which consists of excess of and a small quantity of water. In ordinary language it called a solution of water in phenol. If now the tem- e is raised, this second liquid phase will disappear, and r amount of phenol must be added in order to produce ration of the liquid into two layers. In this way, by ing the amount of phenol and noting the temperature at he two layers disappear, the so-called solubility curve of in water can be obtained. By noting the change of the ty with the temperature in this manner, it is found that emperatures below 68·4°, the addition of more than a amount of phenol causes the formation of two layers; peratures above this, however, two layers cannot be no matter how much phenol is added. At tempera- ove 68·4°, therefore, water and phenol are miscible in ortions.

the other hand, if water is added to phenol at the y temperature, a liquid is produced which consists of phenol, and on increasing the amount of water a certain point, two layers are formed. On raising perature these two layers disappear, and a homogene- ution is again obtained. The phenomena are exactly us to those already described. Since, now, in the second

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Mag., 1884, [5], 18. 22; 495.

[2] *Wied. Annalen*, 1886, 28. 305.

[3] *Zeitschr. physikal. Chem.*, 1898, 26. 433.

case the concentration of the phenol in the solution gra decreases, while in the former case it gradually increa point must at length be reached at which the compositi the two solutions becomes the same. On mixing th solutions, therefore, one homogeneous liquid will be obt But the point at which two phases become identical is a critical point, so that, in accordance with this definitio temperature at which the two solutions of phenol and become identical may be called the *critical solution tempe* and the concentrati this point may be the *critical concentratio*

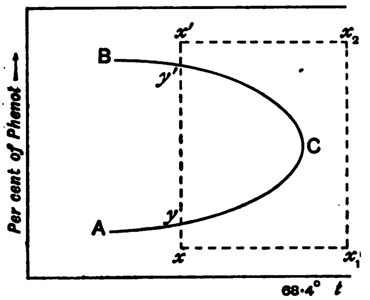

FIG. 22.

From what has bee above, it will be seen t any temperature belo critical solution tempe two conjugate solution taining water and phe different concentratio exist together, one co ing excess of wate other excess of phenol. The following table gives the position of the two layers, and the values are repres graphically in Fig. 22.[1]

PHENOL AND WATER.

C_1 is the percentage amount of phenol in the first layer.
C_2 ,, ,, ,, second layer.

Temperature.	C_1.	C_2.
20°	8·5	72·2
30°	8·7	69·9
40°	9·7	66·8
50°	12·0	62·7
55°	14·2	60·0
60°	17·5	56·2
65°	22·7	49·7
68·4°	36·1	36·1

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[1] Rothmund, *loc. cit.*

The critical solution temperature for phenol and water is °, the critical concentration 36·1 per cent. of phenol. At temperatures above 68·4°, only homogeneous solutions of nol and water can be obtained; water and phenol are then cible in all proportions.

At the critical solution point the system exists in only two ses—liquid and vapour. It ought, therefore, to possess degrees of freedom. The restriction is, however, imposed the composition of the two liquid phases is the same, this disposes of one of the degrees of freedom. The em is therefore univariant; and at a given temperature pressure will have a definite value. Conversely, if the ssure is fixed (as is the case when the system is under the ssure of its own vapour), then the temperature will also be d; that is, the critical solution temperature has a definite ue depending only on the substances. If the vapour phase mitted, the temperature will alter with the pressure; in this e, however, as in the case of other condensed systems, the ct of pressure is slight.

From Fig. 22 it is easy to predict the effect of bringing ether water and phenol in any given quantities at any tem-ature. Start with a solution of phenol and water having the nposition represented by the point *x*. If to this solution enol is added at constant temperature, it will dissolve, and composition of the solution will gradually change, as shown the dotted line *xy*. When, however, the concentration has ached the value represented by the point *y*, two liquid layers ll be formed, the one solution having the composition repre-nted by *y*, the other that represented by *y′*. The system is ow univariant, and on further addition of phenol, the compo-ition of the two liquid phases will remain unchanged, but their elative amounts will alter. The phase richer in phenol will increase in amount; that richer in water will decrease, and ultimately disappear, and there will remain the solution *y′*. Continued addition of phenol will then lead to the point *x′*, there being now only one liquid phase present.

Since the critical solution point represents the highest temperature at which two liquid phases consisting of phenol and water can exist together, these two substances can be br together in any amount whatever at temperatures higher 68·4°, without the formation of two layers. It will the be possible to pass from a system represented by x t represented by x', without at any time two liquid phas pearing. Starting with x, the temperature is first raised the critical solution temperature; phenol is then added the concentration reaches the point x_2. On allowing the perature to fall, the s will then pass into th dition represented b

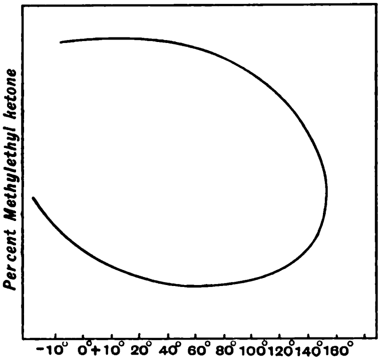

FIG. 23.

Methylethylk and Water.—In the just described, the bility of each comp in the other incr continuously with temperature. There however, cases wh maximum or minim solubility is found methylethylketon water. The curve which represents the equilibria be these two substances is given in Fig. 23, the concent values being contained in the following table:[1]—

METHYLETHYLKETONE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
− 10°	34·5	89·7
+ 10°	26·1	90·0
30°	21·9	89·9
50°	17·5	89·0
70°	16·2	85·7
90°	16·1	84·8
110°	17·7	80·0
130°	21·8	71·9
140°	26·0	64·0
151·8°	44·2	44·2

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[1] Rothmund, *loc. cit.*

iese numbers and Fig. 23 show clearly the occurrence of imum in the solubility of the ketone in water, and also a ıum (at about 10°) in the solubility of water in methyl- etone. Minima of solubility have also been found in cases.

iethylamine and Water.—Although in most of the cases d the solubility of one liquid in another increases with f temperature, this is in all cases. Thus, peratures below 18°, lamine and water gether in all propor- ; but, on raising the rature, the homo- us solution becomes l and separates into yers. In this case, ore, the critical solu- emperature is found direction of lower rature, not in the ion of higher. This behaviour is clearly shown by the ic representation in Fig. 24, and also by the numbers in llowing table :—

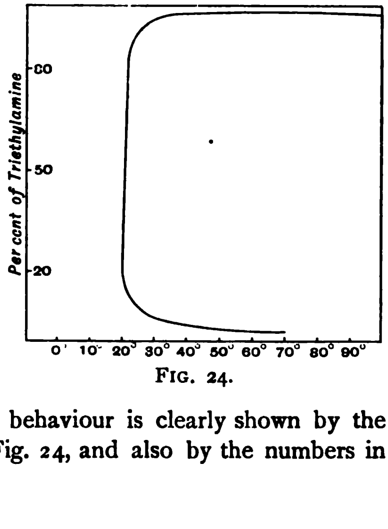

FIG. 24.

TRIETHYLAMINE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
70°	1·6	—
50°	2·9	—
30°	5·6	96
25°	7·3	95·5
20°	15·5	73
± 18·5°	± 30	± 30

Ieneral Form of Concentration-Temperature Curve.— n the preceding figures it will be seen that the general ı of the solubility curve is somewhat parabolic in shape;

in the case of triethylamine and water, the closed end of the curve is very flat. Since for all liquids there is a point (critical point) at which the liquid and gaseous states become identical, and since all gases are miscible in all proportions, it follows that there must be some temperature at which the liquids become perfectly miscible. In the case of triethylamine and water, which has just been considered, there must therefore be an upper critical solution temperature, so that the complete solubility relations would be represented by a closed curve of an ellipsoidal aspect. Although it is possible that this is th general form of the curve for all pairs of liquids, there are a yet insufficient data to prove it.

With regard to the closed end of the curve it may be sai that it is continuous; the critical solution point is not the inte section of two curves, for such a break in the continuity of th curve could occur only if there were some discontinuity in o of the phases. No such discontinuity exists. The curve i therefore, not to be considered as two solubility curves cutti at a point; it is a curve of equilibrium between two co ponents, and so long as the phases undergo continuous change, the curve representing the equilibrium must also be continuou As has already been emphasized, a distinction between solvent and solute is merely conventional (p. 91).

Pressure-Concentration Diagram.—In considering the pressure-concentration diagram of a system of two liquid components, a distinction must be drawn between the tot pressure of the system and the partial pressures of the com ponents. On studying the total pressure of a system, it is found that two cases can be obtained.[1]

So long as there is only one liquid phase, the system is bivariant. The pressure therefore can change with the con centration and the temperature. If the temperature is maintained constant, the pressure will vary only with the concentration and this variation can therefore be represented by a curve If, however, two liquid phases are formed, the system becomes univariant; and if one of the variables, say the temperature, i y fixed, the system no longer possesses any degree of *When two liquid phases are formed, therefore, the tions and the pressure have definite values, which are d so long as the two liquid phases are present;* the ure being supposed constant.

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[1] Konowalow, *Wied. Annalen*, 1881, **14**. 219. Ostwald, *Lehrbuch* II. **2**. 687. Bancroft, *Phase Rule*, p. 96.

ig. 25 is given a diagrammatic representation of the s of pressure-concentration curves which have so far tained. In the , the pressure of riant system (at temperature) lies han the vapour of either of the ponents; a phe- which is very found in the partially miscible *e.g.* ether and Accordingly, by tion of water to r of ether to ere is an increase in the *total* vapour pressure of the

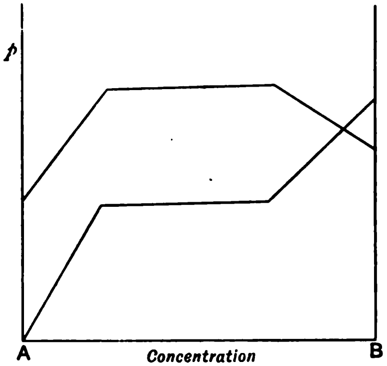

FIG. 25.

regard to the second type, the vapour pressure of ms with two liquid phases lies between that of the le components. An example of this is found in dioxide and water.[2] On adding sulphur dioxide to ere is an increase of the total vapour pressure; but g water to liquid sulphur dioxide, the total vapour is diminished.

case that the vapour pressure of the system with two ases is *less* than that of each of the components is not

regard to the *partial pressure* of the components, the r is more uniform. The partial pressure of one

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owalow, *loc. cit.*

eboom, *Zeitschr. physikal. Chem.*, 1891, 8. 526; *Rec. Trav. ys-Bas*, 1884, 3. 38.

component is in all cases lowered by the addition of the other component, the diminution being approximately proportional to the amount added. If two liquid phases are present, the partial pressure of the components, as well as the total pressure, is constant, and is the same for both phases. That is to say, in the case of the two liquids, saturated solution of water in ether, and of ether in water, the partial pressure of the ether in the vapour in contact with the one solution is the same as that in the vapour over the other solution.[1]

Complete Miscibility.—Although the phenomena of complete miscibility are here treated under a separate heading, it must not be thought that there is any essential difference between those cases where the liquids exhibit limited miscibility and those in which only one homogeneous solution is formed. As has been already pointed out, the solubility relations alter with the temperature; and liquids which at one temperature can dissolve in one another only to a limited extent, are found at some other temperature to possess the property of complete miscibility. Conversely, we may expect that liquids which at one temperature, say at the ordinary temperature, are miscible in all proportions, will be found at some other temperature to be only partially miscible. Thus, for example, it was found by Guthrie that ethyl alcohol and carbon disulphide, which are miscible in all proportions at the ordinary temperature, possess only limited miscibility at temperatures below $-14{\cdot}4^\circ$.[2] Nevertheless, it is doubtful if the critical solution temperature is in all cases experimentally realizable.

Pressure-Concentration Diagram.—Since, in the cases of complete miscibility of two liquid components, there are never more than two phases present, the system must always be bivariant; and two of the variables pressure, temperature or concentration of the components, must be arbitrarily chosen before the system becomes defined. For this reason the Phase Rule affords only a slight guidance in the study of such equilibria; and we shall therefore not enter in detail into the behaviour of these homogeneous mixtures. All that the Phase n tell us in connection with these solutions, is that at t temperature the vapour pressure of the solution varies composition of the liquid phase; and if the composi- the liquid phase remains unchanged, the pressure also main unchanged. This constancy of composition is d not only by pure liquids, but also by liquid solutions ses where the vapour pressure of the solution reaches num or minimum value. This is the case, for example, xtures of constant boiling point.[1]

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[1] Konowalow, *loc. cit.* Cf. Bancroft, *Phase Rule*, p. 100.

[2] *Phil. Mag.*, 1884 [5], **18**. 503.

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for example, Walker, *Introduction to Physical Chemistry*, p. 81 an, 1899). Consult also Young, *Fractional Distillation* (Mac- 903), where the subject is fully treated.

the one passes into the other with change of temperature. The formal separation into two groups is based on the miscibility relations at ordinary temperatures.

Partial or Limited Miscibility.—In accordance with the Phase Rule, a pure liquid in contact with its vapour constitutes a univariant system. If, however, a small quantity of a second substance is added, which is capable of dissolving in the first, a bivariant system will be obtained; for there are now two components and, as before, only two phases—the homogeneous liquid solution and the vapour. At constant temperature, therefore, both the composition of the solution and the pressure of the vapour can undergo change; or, if the composition of the solution remains unchanged, the pressure and the temperature can alter. If the second (liquid) component is added in increasing amount, the liquid will at first remain homogeneous, and its composition and pressure will undergo a continuous change; when, however, the concentration has reached a definite value, solution no longer takes place; two liquid phases are produced. Since there are now three phases present, two liquids and vapour, the system is univariant; at a given temperature, therefore, the concentration of the components in the two liquid phases, as well as the vapour pressure, must have definite values. Addition of one of the components, therefore, cannot alter the concentrations or the pressure, but can only cause a change in the relative amounts of the phases.

The two liquid phases can be regarded, the one as a solution of the component I. in component II., the other as a solution of component II. in component I. If the pressure is maintained constant, then to each temperature there will correspond a definite concentration of the components in the two liquid phases; and addition of excess of one will merely alter the relative amounts of the two solutions. As the temperature changes, the composition of the two solutions will change, and there will therefore be obtained two solubility curves, one showing the solubility of component I. in component II., the other showing the solubility of component II. in component I. Since heat may be either evolved or absorbed when one liquid dissolves in another, the solubility may diminish or increase vapour will condense to liquid, in order that the pressure may remain constant, and so much of the solid will pass into solution that the concentration may remain unchanged; for, so long as the three phases are present, the state of the system cannot alter. If, however, one of the phases, *e.g.* the vapour phase, disappears, the system becomes bivariant; at any given temperature, therefore, there may be different values of concentration and pressure.

The direction in which change of concentration will occur with change of pressure can be predicted by means of the theorem of Le Chatelier, if it is known whether solution is accompanied by increase or diminution of the total volume. If a solid dissolves with diminution of volume, increase of pressure will increase the solubility; in the reverse case, increase of pressure will diminish the solubility.

This conclusion has also been verified by experiment, as is shown by the following figures.[1]

Salt.	Change of volume by dissolving 1 gm. of salt in the saturated solution.	Solubility (at 18°) (grams salt in 1 gram of solution).	
		Pressure = 1 atm.	Pressure = 500 atm.
Sodium chloride . . .	−0·07	0·264	0·270
Ammonium chloride . .	+0·10	0·272	0·258
Alum	−0·067	0·115	0·142 (p = 400 atm.)

As can be seen, a large increase of the pressure brings about a no more than appreciable alteration of the solubility; a result which is due, as in the case of the alteration of the fusion point with the pressure, to the small change in volume accompanying solution or increase of pressure. For all practical purposes, therefore, the solubility as determined under atmospheric pressure may be taken as equal to the true case the concentration of the phenol in the solution grad decreases, while in the former case it gradually increas point must at length be reached at which the compositio the two solutions becomes the same. On mixing the solutions, therefore, one homogeneous liquid will be obtai But the point at which two phases become identical is c a critical point, so that, in accordance with this definitio temperature at which the two solutions of phenol and become identical may be called the *critical solution temper* and the concentratio this point may be the *critical concentratio*

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[1] E. von Stackelberg, *Zeitschr. physikal. Chem.*, 1896, **20**. 337. If the hange of volume which accompanies solution, and the heat effect are nown, the quantitative change of the solubility with the pressure can be lculated (Braun, *Zeitschr. physikal. Chem.*, 1887, **1**. 259).

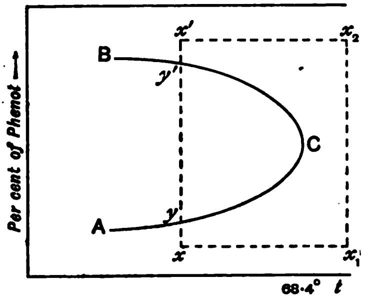

FIG. 22.

From what has bee above, it will be seen t any temperature belo critical solution temper two conjugate solution taining water and phe different concentratio exist together, one co ing excess of wate other excess of phenol. The following table gives the position of the two layers, and the values are repres graphically in Fig. 22.[1]

PHENOL AND WATER.

C_1 is the percentage amount of phenol in the first layer.
C_2 ,, ,, ,, second layer.

Temperature.	C_1.	C_2.
20°	8·5	72·2
30°	8·7	69·9
40°	9·7	66·8
50°	12·0	62·7
55°	14·2	60·0
60°	17·5	56·2
65°	22·7	49·7
68·4°	36·1	36·1

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[1] Rothmund, *loc. cit.*

ıe critical solution temperature for phenol and water is the critical concentration 36·1 per cent. of phenol. At nperatures above 68·4°, only homogeneous solutions of ! and water can be obtained; water and phenol are then le in all proportions.

the critical solution point the system exists in only two –liquid and vapour. It ought, therefore, to possess grees of freedom. The restriction is, however, imposed e composition of the two liquid phases is the same, s disposes of one of the degrees of freedom. The is therefore univariant; and at a given temperature ssure will have a definite value. Conversely, if the : is fixed (as is the case when the system is under the : of its own vapour), then the temperature will also be hat is, the critical solution temperature has a definite epending only on the substances. If the vapour phase ed, the temperature will alter with the pressure; in this owever, as in the case of other condensed systems, the f pressure is slight.

m Fig. 22 it is easy to predict the effect of bringing r water and phenol in any given quantities at any tem-e. Start with a solution of phenol and water having the ition represented by the point *x*. If to this solution is added at constant temperature, it will dissolve, and nposition of the solution will gradually change, as shown dotted line *xy*. When, however, the concentration has the value represented by the point *y*, two liquid layers formed, the one solution having the composition repre-by *y*, the other that represented by *y'*. The system is ivariant, and on further addition of phenol, the compo-f the two liquid phases will remain unchanged, but their amounts will alter. The phase richer in phenol will e in amount; that richer in water will decrease, and ely disappear, and there will remain the solution *y'*. ued addition of phenol will then lead to the point *x'*, eing now only one liquid phase present.

ce the critical solution point represents the highest tem-e at which two liquid phases consisting of phenol and case the concentration of the phenol in the solution gradually decreases, while in the former case it gradually increases, a point must at length be reached at which the composition of the two solutions becomes the same. On mixing the two solutions, therefore, one homogeneous liquid will be obtained. But the point at which two phases become identical is called a critical point, so that, in accordance with this definition, the temperature at which the two solutions of phenol and water become identical may be called the *critical solution temperature*, and the concentration at this point may be called the *critical concentration*.

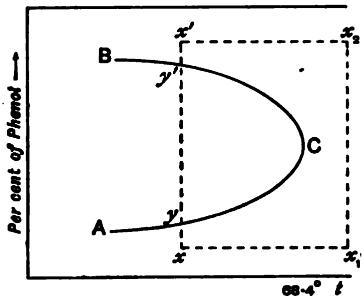

FIG. 22.

From what has been said above, it will be seen that at any temperature below the critical solution temperature, two conjugate solutions containing water and phenol in different concentration can exist together, one containing excess of water, the other excess of phenol. The following table gives the composition of the two layers, and the values are represented graphically in Fig. 22.[1]

PHENOL AND WATER.

C_1 is the percentage amount of phenol in the first layer.
C_2 „ „ „ second layer.

Temperature.	C_1.	C_2.
20°	8·5	72·2
30°	8·7	69·9
40°	9·7	66·8
50°	12·0	62·7
55°	14·2	60·0
60°	17·5	56·2
65°	22·7	49·7
68·4°	36·1	36·1

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[1] Rothmund, *loc. cit.*

The critical solution temperature for phenol and water is 8·4°, the critical concentration 36·1 per cent. of phenol. At ll temperatures above 68·4°, only homogeneous solutions of henol and water can be obtained; water and phenol are then miscible in all proportions.

At the critical solution point the system exists in only two phases—liquid and vapour. It ought, therefore, to possess two degrees of freedom. The restriction is, however, imposed that the composition of the two liquid phases is the same, and this disposes of one of the degrees of freedom. The system is therefore univariant; and at a given temperature the pressure will have a definite value. Conversely, if the pressure is fixed (as is the case when the system is under the pressure of its own vapour), then the temperature will also be fixed; that is, the critical solution temperature has a definite value depending only on the substances. If the vapour phase is omitted, the temperature will alter with the pressure; in this case, however, as in the case of other condensed systems, the effect of pressure is slight.

From Fig. 22 it is easy to predict the effect of bringing together water and phenol in any given quantities at any temperature. Start with a solution of phenol and water having the composition represented by the point *x*. If to this solution phenol is added at constant temperature, it will dissolve, and the composition of the solution will gradually change, as shown by the dotted line *xy*. When, however, the concentration has reached the value represented by the point *y*, two liquid layers will be formed, the one solution having the composition represented by *y*, the other that represented by *y'*. The system is now univariant, and on further addition of phenol, the composition of the two liquid phases will remain unchanged, but their relative amounts will alter. The phase richer in phenol will increase in amount; that richer in water will decrease, and ltimately disappear, and there will remain the solution *y'*. Continued addition of phenol will then lead to the point *x'*, here being now only one liquid phase present.

Since the critical solution point represents the highest temperature at which two liquid phases consisting of phenol and water can exist together, these two substances can be brought together in any amount whatever at temperatures higher than 68·4°, without the formation of two layers. It will therefore be possible to pass from a system represented by x to one represented by x', without at any time two liquid phases appearing. Starting with x, the temperature is first raised above the critical solution temperature; phenol is then added until the concentration reaches the point x_2. On allowing the temperature to fall, the system will then pass into the condition represented by x'.

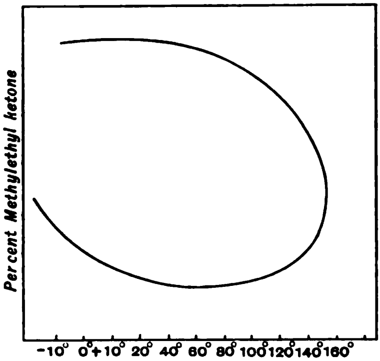

FIG. 23.

Methylethylketone and Water.—In the case just described, the solubility of each component in the other increased continuously with the temperature. There are, however, cases where a maximum or minimum of solubility is found, *e.g.* methylethylketone and water. The curve which represents the equilibria between these two substances is given in Fig. 23, the concentration values being contained in the following table:[1]—

METHYLETHYLKETONE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
− 10°	34·5	89·7
+ 10°	26·1	90·0
30°	21·9	89·9
50°	17·5	89·0
70°	16·2	85·7
90°	16·1	84·8
110°	17·7	80·0
130°	21·8	71·9
140°	26·0	64·0
151·8°	44·2	44·2

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[1] Rothmund, *loc. cit.*

These numbers and Fig. 23 show clearly the occurrence of a minimum in the solubility of the ketone in water, and also a minimum (at about 10°) in the solubility of water in methylethylketone. Minima of solubility have also been found in other cases.

Triethylamine and Water.—Although in most of the cases studied the solubility of one liquid in another increases with rise of temperature, this is not so in all cases. Thus, at temperatures below 18°, riethylamine and water nix together in all proporions; but, on raising the emperature, the homogeneous solution becomes urbid and separates into wo layers. In this case, herefore, the critical soluion temperature is found n the direction of lower mperature, not in the irection of higher. This behaviour is clearly shown by the aphic representation in Fig. 24, and also by the numbers in e following table:—

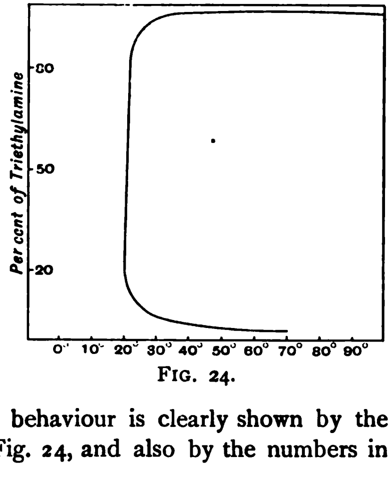

FIG. 24.

TRIETHYLAMINE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
70°	1·6	—
50°	2·9	—
30°	5·6	96
25°	7·3	95·5
20°	15·5	73
± 18·5°	± 30	± 30

General Form of Concentration-Temperature Curve.—m the preceding figures it will be seen that the general n of the solubility curve is somewhat parabolic in shape;

in the case of triethylamine and water, the closed end of the curve is very flat. Since for all liquids there is a point (critical point) at which the liquid and gaseous states become identical, and since all gases are miscible in all proportions, it follows that there must be some temperature at which the liquids become perfectly miscible. In the case of triethylamine and water, which has just been considered, there must therefore be an upper critical solution temperature, so that the complete solubility relations would be represented by a closed curve of an ellipsoidal aspect. Although it is possible that this is the general form of the curve for all pairs of liquids, there are as yet insufficient data to prove it.

With regard to the closed end of the curve it may be said that it is continuous; the critical solution point is not the intersection of two curves, for such a break in the continuity of the curve could occur only if there were some discontinuity in one of the phases. No such discontinuity exists. The curve is, therefore, not to be considered as two solubility curves cutting at a point; it is a curve of equilibrium between two components, and so long as the phases undergo continuous change, the curve representing the equilibrium must also be continuous. As has already been emphasized, a distinction between solvent and solute is merely conventional (p. 91).

Pressure - Concentration Diagram.—In considering the pressure-concentration diagram of a system of two liquid components, a distinction must be drawn between the total pressure of the system and the partial pressures of the components. On studying the total pressure of a system, it is found that two cases can be obtained.[1]

So long as there is only one liquid phase, the system is bivariant. The pressure therefore can change with the concentration and the temperature. If the temperature is maintained constant, the pressure will vary only with the concentration, and this variation can therefore be represented by a curve. If, however, two liquid phases are formed, the system becomes univariant; and if one of the variables, say the temperature, is y fixed, the system no longer possesses any degree of *When two liquid phases are formed, therefore, the tions and the pressure have definite values, which are ed so long as the two liquid phases are present;* the ure being supposed constant.

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[1] Konowalow, *Wied. Annalen*, 1881, **14**. 219. Ostwald, *Lehrbuch*, II. **2**. 687. Bancroft, *Phase Rule*, p. 96.

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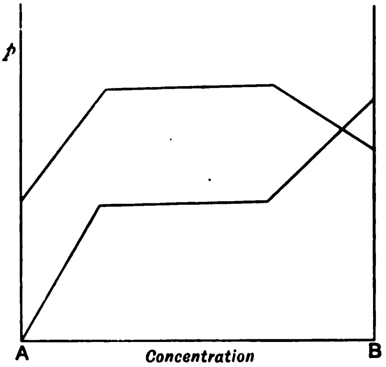

FIG. 25.

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component is in all cases lowered by the addition of the other component, the diminution being approximately proportional to the amount added. If two liquid phases are present, the partial pressure of the components, as well as the total pressure, is constant, and is the same for both phases. That is to say, in the case of the two liquids, saturated solution of water in ether, and of ether in water, the partial pressure of the ether in the vapour in contact with the one solution is the same as that in the vapour over the other solution.[1]

Complete Miscibility.—Although the phenomena of complete miscibility are here treated under a separate heading, it must not be thought that there is any essential difference between those cases where the liquids exhibit limited miscibility and those in which only one homogeneous solution is formed. As has been already pointed out, the solubility relations alter with the temperature; and liquids which at one temperature can dissolve in one another only to a limited extent, are found at some other temperature to possess the property of complete miscibility. Conversely, we may expect that liquids which at one temperature, say at the ordinary temperature, are miscible in all proportions, will be found at some other temperature to be only partially miscible. Thus, for example, it was found by Guthrie that ethyl alcohol and carbon disulphide, which are miscible in all proportions at the ordinary temperature, possess only limited miscibility at temperatures below −14·4°.[2] Nevertheless, it is doubtful if the critical solution temperature is in all cases experimentally realizable.

Pressure-Concentration Diagram.—Since, in the cases of complete miscibility of two liquid components, there are never more than two phases present, the system must always be bivariant; and two of the variables pressure, temperature or concentration of the components, must be arbitrarily chosen before the system becomes defined. For this reason the Phase Rule affords only a slight guidance in the study of such equilibria; and we shall therefore not enter in detail into the behaviour of these homogeneous mixtures. All that the Phase an tell us in connection with these solutions, is that at nt temperature the vapour pressure of the solution varies e composition of the liquid phase; and if the composi- the liquid phase remains unchanged, the pressure also emain unchanged. This constancy of composition is ed not only by pure liquids, but also by liquid solutions ases where the vapour pressure of the solution reaches mum or minimum value. This is the case, for example, ixtures of constant boiling point.[1]

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[1] Konowalow, *loc. cit.* Cf. Bancroft, *Phase Rule*, p. 100.

[2] *Phil. Mag.*, 1884 [5], **18**. 503.

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CHAPTER VII

SOLUTIONS OF SOLIDS IN LIQUIDS, ONLY ONE OF THE COMPONENTS BEING VOLATILE

General.—When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into solution; and the process continues until the concentration reaches a definite value independent of the amount of solid present. A condition of equilibrium is established between the solid and the solution; the solution becomes *saturated*. Since the number of components is two, and the number of phases three, viz. solid, liquid solution, vapour, the system is univariant. If, therefore, one of the factors, pressure, temperature, or concentration of the components (in the solution[1]), is arbitrarily fixed, the state of the system becomes perfectly defined. Thus, at any given temperature, the vapour pressure of the system and the concentration of the components have a definite value. If the temperature is altered, the vapour pressure and also, in general, the concentration will undergo change. Likewise, if the pressure varies, while the system is isolated so that no heat can pass between it and its surroundings, the concentration and the temperature must also undergo variation until they attain values corresponding to the particular pressure.

That the temperature has an influence, sometimes a very considerable influence, on the amount of substance passing into solution, is sufficiently well known; the effect of pressure, although less apparent, is no less certain. If at any given temperature the volume of the vapour phase is diminished, pour will condense to liquid, in order that the pressure may main constant, and so much of the solid will pass into soluon that the concentration may remain unchanged; for, so ng as the three phases are present, the state of the system nnot alter. If, however, one of the phases, *e.g.* the vapour hase, disappears, the system becomes bivariant; at any given mperature, therefore, there may be different values of conentration and pressure.

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[1] Since this is the only phase of variable composition present.

The direction in which change of concentration will occur ith change of pressure can be predicted by means of the heorem of Le Chatelier, if it is known whether solution is ccompanied by increase or diminution of the total volume. If a solid dissolves with diminution of volume, increase of pressure will increase the solubility; in the reverse case, increase of pressure will diminish the solubility.

This conclusion has also been verified by experiment, as is shown by the following figures.[1]

Salt.	Change of volume by dissolving 1 gm. of salt in the saturated solution.	Solubility (at 18°) (grams salt in 1 gram of solution).	
		Pressure = 1 atm.	Pressure = 500 atm.
Sodium chloride . . .	−0·07	0·264	0·270
Ammonium chloride . .	+0·10	0·272	0·258
Alum	−0·067	0·115	0·142 (p = 400 atm.)

As can be seen, a large increase of the pressure brings about a no more than appreciable alteration of the solubility; a result which is due, as in the case of the alteration of the fusion point with the pressure, to the small change in volume accompanying solution or increase of pressure. For all practical purposes, therefore, the solubility as determined under atmospheric pressure may be taken as equal to the true

[1] E. von Stackelberg, *Zeitschr. physikal. Chem.*, 1896, **20**. 337. If the change of volume which accompanies solution, and the heat effect are known, the quantitative change of the solubility with the pressure can be calculated (Braun, *Zeitschr. physikal. Chem.*, 1887, **1**. 259).

solubility, that is, the solubility when the system is under the pressure of its own vapour.

The Saturated Solution.—From what has been said above, it will be seen that the condition of saturation of a solution can be defined only with respect to a certain solid phase; if no solid is present, the system is undefined, for it then consists of only two phases, and is therefore bivariant. Under such circumstances not only can there be at one given temperature solutions of different concentration, all containing less of one of the components than when that component is present in the solid form, but there can also exist solutions containing more of that component than corresponds to the equilibrium when the solid is present. In the former case the solutions are *unsaturated*, in the latter case they are *supersaturated with respect to a certain solid phase;* in themselves, the solutions are stable, and are neither unsaturated nor supersaturated. Further, if the solid substance can exist in different allotropic modifications, the particular form of the substance which is in equilibrium with the solution must be known, in order that the statement of the solubility may be definite; for each form has its own solubility, and, as we shall see presently, the less stable form has the greater solubility (cf. p. 45). In all determinations of the solubility, therefore, not only must the concentration of the components in the solution be determined, but equal importance should be attached to the characterisation of the solid phase present.

In this connection, also, one other point may be emphasised. For the production of the equilibrium between a solid and a liquid, time is necessary, and this time not only varies with the state of division of the solid and the efficiency of the stirring, but is also dependent on the nature of the substance.[1] Considerable care must therefore be taken that sufficient time is allowed for equilibrium to be established. Such care is more especially needful when changes may occur in the solid phase, and neglect of it has greatly diminished the value of many of the older determinations of solubility.

Form of the Solubility Curve.—The solubility curve—that is, the curve representing the change of concentration of the components in the solution with the temperature—differs markedly from the curve of vapour pressure (p. 61), in that it possesses no general form, but may vary in the most diverse manner. Not only may the curve have an almost straight and horizontal course, or slope or curve upwards at varying angles; but it may even slope downwards, corresponding to a decrease in the solubility with rise of temperature; may exhibit maxima or minima of solubility, or may, as in the case of some hydrated salts, pass through a point of maximum temperature. In the latter case the salt may possess two values of solubility at the same temperature. We shall consider these cases in the following chapter.

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[1] Van't Hoff, *Arch. néerland.* 1901 [2], 6. 471.

The great variety of form shown by solubility curves is at once apparent from Fig. 26, in which the solubility curves of various substances (not, however, drawn to scale) are reproduced.[1]

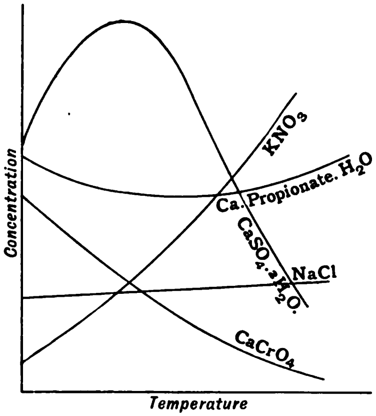

FIG. 26.

Varied as is the form of the solubility curve, its *direction*, nevertheless, can be predicted by means of the theorem of van't Hoff and Le Chatelier; for in accordance with that theorem (p. 55) increase of solubility with the temperature must occur in those cases where the process of solution is accompanied by an *absorption* of heat; and a decrease in the solubility with rise of temperature will be found in cases where solution occurs with *evolution* of heat. Where there is no heat effect accompanying solution, change of temperature will be without influence on the bility; and if the sign of the heat of solution change direction of the solubility curve must also change, *i.e.* show a maximum or minimum point. This has in all been verified by experiment.[1]

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[1] Tilden and Shenstone, *Phil. Trans.* 1884, **175**. 23; Hulett and Allen, *Jour. Amer. Chem. Soc.* 1902, **24**. 667; Andreä, *Jour. prak. Chem.* **137**. 474; Lumsden, *Jour. Chem. Soc.*, 1902, **81**. 350; Mylius and v. Wrochem, *Ber.* 1900, **33**. 3689.

In applying the theorem of Le Chatelier to the cou the solubility curve, it should be noted that by heat of so there is meant, not the heat effect produced on dissolvi salt in a large amount of solvent (which is the usual signifi of the expression), but the heat which is absorbed or ev when the salt is dissolved in the almost saturated solutio so-called last heat of solution). Not only does the heat in the two cases have a different value, but it may even a different sign. A striking example of this is afford cupric chloride, as the following figures show:[2]—

Number of gram-molecules of $CuCl_2, 2H_2O$ dissolved in 198 gram-molecules of water.	Heat effect.
1	+37 K
2·02	+66 ,,
4·15	+105 ,,
7·07	+117 ,,
9·95	+117 ,,
11	+91 ,,
18·8	−10 ,,
19·6	−31 ,,
24·75	−198 ,,

In the above table the positive sign indicates evolut heat, the negative sign, absorption of heat; and the val the heat effect are expressed in centuple calories. J from the heat effect produced on dissolving cupric chlo a large bulk of water, we should predict that the solubi that salt would diminish with rise of temperature; as a of fact, it increases. This is in accordance with the fa e last heat of solution is *negative* (as expressed above), *i.e.* lution of the salt in the almost saturated solution is accom-anied by absorption of heat. We are led to expect this from e fact that the heat of solution changes sign from positive o negative as the concentration increases; experiment also howed it to be the case

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[1] E. von Stackelberg, *Zeitschr. physikal. Chem.* 1896, **20.** 159; 533; Lumsden, *Jour. Chem. Soc.*, 1902, **81.** 350; Holsboer, *physikal. Chem.*, 1902, **39.** 691.

[2] Reicher and van Deventer, *Zeitschr. physikal. Chem.* 1890, **5.** Ostwald, *Lehrbuch*, II. **2.** 803.

Despite its many forms, it should be particularly noted that he solubility curve of any substance is *continuous*, so long as he solid phase, or solid substance in contact with the solution, remains unchanged. If any "break" or discontinuous change in the direction of the curve occurs, it is a sign that the *solid phase has undergone alteration.* Conversely, if it is known that a change takes place in the solid phase, a break in the solubility curve can be predicted. We shall presently meet with examples of this.[1]

A.—ANHYDROUS SALT AND WATER.

The Solubility Curve.—In studying the equilibria in those systems of two components in which the liquid phase is a solution or phase of varying composition, we shall in the present chapter limit the discussion to those cases where no compounds are formed, but where the components crystallise out in the pure state. Since some of the best-known examples of such systems are yielded by the solutions of anhydrous salts in water, we shall first of all briefly consider some of the results which have been obtained with them.

For the most part the solubility curves have been studied only at temperatures lying between 0° and 100°, the solid phase in contact with the solution being the anhydrous salt. For the representation of these equilibria, the concentration-temperature

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[1] It has been shown that the formula of Ramsay and Young (p. 64) can be applied (with certain restrictions) to the interpolation and extrapolation of the solubility curve of a substance provided two (or three) points on the curve are known. In this case T, T_1, etc., refer to the temperatures at which the two substances—one the solubility curve of which is known, the other the solubility curve of which is to be calculated—have equal solubilities, instead of, as in the previous case, equal vapour pressures. Findlay, *Proc. Roy. Soc.*, 1902, **69.** 471; *Zeitschr. physikal. Chem.*, 1903, **2.** 110.)

diagram is employed, the concentration being express
number of grams of the salt dissolved in 100 grams
or as the number of gram-molecules of salt in 10
molecules of water. The curves thus obtained ex
different forms to which reference has already been m
long as the salt remains unchanged the curve will be co
but if the salt alters its form, then the solubility curve
a break.

Now, we have already seen in Chapter III. tha
substances are capable of existing in various crystalli
and these forms are so related to one another that a
temperature the relative stability of each pair of pol
forms undergoes change. Since each crystalline var
substance must have its own solubility, there must be
in the solubility curve at the temperature of transitio
two enantiotropic forms. At this point the two
curves must cut, for since the two forms are in eq
with respect to their vapour, they must also be in eq
with respect to their solutions. From the table on
is seen that potassium nitrate, ammonium nitrate, silve
thallium nitrate, thallium picrate, are capable of existin
or more different
tropic crystalline fo
range of stability
forms being limited
nite temperatures (t
temperature). Since
sition point is not al
a solvent (provided t
is not absorbed by
phase), we should
studying the solu
these substances i
that the solubility cur
exhibit a change in
at the temperature of transition. As a matter of fact
been verified, more especially in the case of ammonium

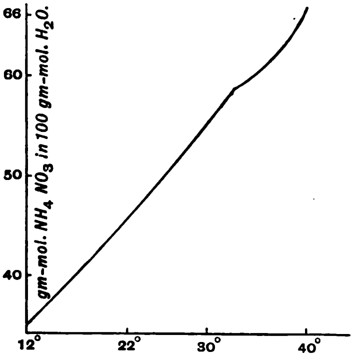

FIG. 27.

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[1] W. Müller and P. Kaufmann, *Zeitschr. physikal. Chem.* 1903,

and thallium picrate.[1] The following table contains the values of the solubility of ammonium nitrate obtained by Müller and Kaufmann, the solubility being expressed in gram-molecules NH_4NO_3 in 100 gram-molecules of water. In Fig. 27 these results are represented graphically. The equilibrium point was approached both from the side of unsaturation and of supersaturation, and the condition of equilibrium was controlled by determinations of the density of the solution.

SOLUBILITY OF AMMONIUM NITRATE.

Temperature.	Solubility.	Temperature.	Solubility.
12·2°	34·50	32·7°	57·90
20·2°	43·30	34·0°	58·89
25·05°	48·19	35·0°	59·80
28·0°	51·86	36·0°	61·00
30·0°	54·40	37·5°	62·90
30·2°	54·61	38·0°	63·60
31·9°	57·20	39·0°	65·09
32·1°	57·60	40·0°	66·80

From the graphic representation of the solubility given in Fig. 27, there is seen to be a distinct change in the direction of the curve at a temperature of 32°; and this break in the curve corresponds to the transition of the β-rhombic into the α-rhombic form of ammonium nitrate (p. 61).

Suspended Transformation and Supersaturation.—As has already been learned, the transformation of the one crystalline form into the other does not necessarily take place immediately the transition point has been passed; and it has therefore been found possible in a number of cases to follow the solubility curve of a given crystalline form beyond the point at which it ceases to be the most stable modification. Now, it will be readily seen from Fig. 27 that if the two solubility curves be prolonged beyond the point of intersection, the solubility of the less stable form is greater than that of the more stable. A solution, therefore, which is saturated with respect to the less stable form, *i.e.* which is in equilibrium with that form, is

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[1] W. O. Rabe, *Zeitschr. physikal. Chem.* 1901, **38**. 175.

supersaturated with respect to the more stable modification. If, therefore, a small quantity of the more stable form is introduced into the solution, the latter must deposit such an amount of the more stable form that the concentration of the solution corresponds to the solubility of the stable form at the particular temperature. Since, however, the solution is now *unsaturated* with respect to the less stable variety, the latter, if present, must pass into solution; and the two processes, deposition of the stable and solution of the metastable form, must go on until the latter form has entirely disappeared and a saturated solution of the stable form is obtained. There will thus be a conversion, through the medium of the solvent, of the less stable into the more stable modification. This behaviour is of practical importance in the determination of transition points (*v.* Appendix).

From the above discussion it will be seen how important the statement of the solid phase is for the definition of saturation and supersaturation.

Solubility Curve at Higher Temperatures.—On passing to the consideration of the solubility curves at higher temperatures, two chief cases must be distinguished.

(1) The two components in the fused state can mix in all proportions.

(2) The two components in the fused state cannot mix in all proportions.

1. *Complete Miscibility of the Fused Components.*

The best example of this which has been studied, so far as anhydrous salts and water are concerned, is that of silver

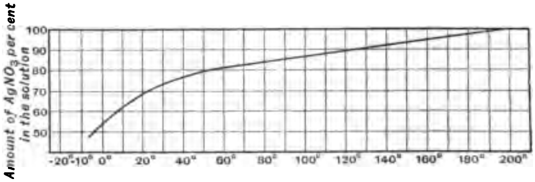

FIG. 28.

nitrate and water. The solubility of this salt at temperatures above 100° has been studied chiefly by Etard [1] and by Tilden and Shenstone.[2] The values obtained by Etard are given in the following table, and represented graphically in Fig. 28.

SOLUBILITY OF SILVER NITRATE.

Temperature.	Parts of dry salt in 100 parts of solution.
−7°	46·2
−1°	52·1
+5°	56·3
10°	61·2
20°	67·8
40·5°	76·8
73°	84·0
135°	92·8
182°	96·9

In this figure the composition of the solution is expressed in parts of silver nitrate in 100 parts by weight of the solution, so that 100 per cent. represents pure silver nitrate. As can be seen, the solubility increases with the temperature. At a temperature of about 160° there should be a break in the curve due to change of crystalline form (p. 61). Such a change in the direction of the solubility curve, however, does not in any way alter the essential nature of the relationships discussed here, and may for the present be left out of account. On following the solubility curve of silver nitrate to higher temperatures, therefore, the concentration of silver nitrate in the solution gradually increases, until at last, at a temperature of 208°,[3] the melting point of pure silver nitrate is reached, and the concentration of the water has become zero. The curve hroughout its whole extent represents the equilibrium between ilver nitrate, solution, and vapour. Conversely, starting with ure silver nitrate in contact with the fused salt, addition of ater will lower the melting point, *i.e.* will lower the temperaure at which the solid salt can exist in contact with the liquid;

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[1] *Annales chim. phys.*, 1894 [7], **2**. 524.

[2] *Phil. Trans.*, 1884, **175**. 23.

[3] Hissink, *Zeitschr. physikal. Chem.*, 1900, **32**. 543.

and the depression will be all the greater the larger the amount of water added. As the concentration of the water in the liquid phase is increased, therefore, the system will pass back along the curve from higher to lower temperatures, and from greater to smaller concentrations of silver nitrate in the liquid phase. The curve in Fig. 28 may, therefore, be regarded either as the solubility curve of silver nitrate in water, or as the freezing point curve for silver nitrate in contact with a solution consisting of that salt and water.

As the temperature of the saturated solution falls, silver nitrate is deposited, and on lowering the temperature sufficiently a point will at last be reached at which ice also begins to separate out. Since there are now four phases co-existing, viz. silver nitrate, ice, solution, vapour, the system is invariant, and the point is a *quadruple point*. This quadruple point, therefore, forms the lower limit of the solubility curve of silver nitrate. Below this point the solution becomes metastable.

Ice as Solid Phase.—Ice melts or is in equilibrium with water at a temperature of 0°. The melting point, will, however, be lowered by the solution of silver nitrate in the water; and the greater the concentration of the salt in the solution the greater will be the depression of the temperature of equilibrium. On continuing the addition of silver nitrate, a point will at length be reached at which the salt is no longer dissolved, but remains in the solid form along with the ice. We again obtain, therefore, the invariant system ice—salt—solution—vapour. The temperature at which this invariant system can exist has been found by Middelberg[1] to be $-7·3°$, the solution at this point containing 47·1 per cent. of silver nitrate.

The same general behaviour will be found in the case of all other systems of two components belonging to this class; that is, in the case of systems from which the components crystallise out in the pure state, and in which the fused components are miscible in all proportions. In all such cases, therefore, the solubility curves (curves of equilibrium) can be represented diagrammatically as in Fig. 29. In this figure OA represents the solubility curve of the salt, and OB the freezing

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[1] *Zeitschr. physikal. Chem.*, 1903, **43**, 313.

:urve of ice. O is the quadruple point at which the at system exists, and may be regarded as the point of :tion of the solucurve with the ; - point curve. ıis point is fixed, ındition of the as regards teme, vapour presıd concentration components (or ıition of the sois perfectly de- From the way, also, in which the condition is attained, dent that the quadruple point is the lowest temperature ı be obtained with mixtures of the two components in :e of vapour. It is known as the *cryohydric point*, or, ly, the *eutectic point*.[1]

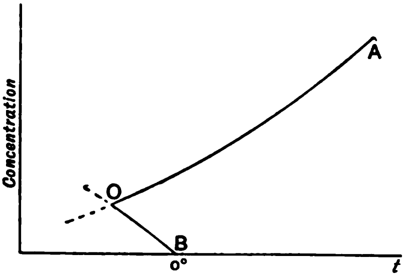

FIG. 29.

ohydrates.[2]—On cooling a solution of common salt in › a temperature of -3°, Guthrie observed that the hydrate H_2O separated out. This salt continued to be deuntil at a temperature of -22° opaque crystals made ppearance, and the liquid passed into the solid state change of temperature. A similar behaviour was ›y Guthrie in the case of a large number of other salts, erature below that of the melting point of ice being l at which on continued withdrawal of heat, the solution :d at a constant temperature. When the system had l this minimum temperature, it was found that the ition of the solid and the liquid phases was the same, ıained unchanged throughout the period of solidification. shown by the following figures, which give the comı of different samples of the solid phase deposited from ıtion at constant temperature.[3]

:hrie, *Phil. Mag.*, 1875, [4], **49.** 1 ; 1884, [5], **17.** 462.

Roloff, *Zeitschr. physikal. Chem.*, 1895, **17.** 325 ; Guthrie,

:hrie, *Phil. Mag.*, *loc. cit.* Cf. Ostwald, *Lehrbuch*, II. **2.** 843.

No.	Temperature of solidification.	NaCl. Per cent.
1	− 21° to − 22°	23·72
2	− 22°	23·66
3	− 22°	23·73
4	− 23°	23·82
5	− 23°	23·34
6	− 23°	23·35
	Mean	23·6

Conversely, a mixture of ice and salt containing cent. of sodium chloride will melt at a definite and temperature, and exhibit, therefore, a behaviour sup be characteristic of a pure chemical compound. Th combined with the fact that the solid which was d was crystalline, and that the same constant tempera attained, no matter with what proportions of water one started, led Guthrie to the belief that the soli thus separated at constant temperature were definite compounds, to which he gave the general name *cry* A large number of such cryohydrates were prepa analysed by Guthrie, and a few of these are give following table, together with the temperature of the cr point:[1]—

CRYOHYDRATES.

Salt.	Cryohydric point.	Percentage o salt in the c
Sodium bromide	− 24°	41·
Sodium chloride	− 22°	23·
Potassium iodide	− 22°	52·
Sodium nitrate	− 17·5°	40·
Ammonium sulphate . .	− 17°	41·
Ammonium chloride . .	− 15°	19·
Sodium iodide	− 15°	59·
Potassium bromide . . .	− 13°	32
Potassium chloride . . .	− 11·4°	20
Magnesium sulphate . .	− 5°	21
Potassium nitrate . . .	− 2·6°	11
Sodium sulphate	− 0·7°	4

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[1] Guthrie, *Phil. Mag.*, 1875 [4], **49**. 269.

The chemical individuality of these cryohydrates was, wever, called in question by Pfaundler,[1] and disproved by ffer,[2] who showed that in spite of the constancy of the melt-g point, the cryohydrates had the properties, not of definite hemical compounds, but of mixtures; the arguments given eing that the heat of solution and the specific volume are he same for the cryohydrate as for a mixture of ice and salt f the same composition; and it was further shown that the ryohydrate had not a definite crystalline form, but separated out as an opaque mass containing the two components in close juxtaposition. The heterogeneous nature of cryohydrates can also be shown by a microscopical examination.

At the cryohydric point, therefore, we are not dealing with a single solid phase, but with two solid phases, ice and salt; the cryohydric point, therefore, as already stated, is a quadruple point and represents an invariant system.

Although on cooling a solution to the cryohydric point, separation of ice may occur, it will not necessarily take place; the system may become metastable. Similarly, separation of salt may not take place immediately the cryohydric point is reached. It will, therefore, be possible to follow the curves BO and AO beyond the quadruple point,[3] which is thereby clearly seen to be the point of intersection of the solubility curve of the salt and the freezing-point curve of ice. At this point, also, the curves of the univariant systems ice—salt—vapour and ice—salt—solution intersect.

Changes at the Quadruple Point.—Since the invariant system ice—salt—solution—vapour can exist only at a definite temperature, addition or withdrawal of heat must cause the disappearance of one of the phases, whereby the system will become univariant. So long as all four phases are present the temperature, pressure, and concentration of the components in the solution must remain constant. When, therefore, heat is added to or withdrawn from the system, mutually compensatory changes will take place within the system whereby the condition of the latter is preserved. These changes can in all cases be foreseen with the help of the theorem of van't Hoff and Le Chatelier; and, after what was said in Chap. IV., need only be briefly referred to here. In the first place, addition of heat will cause ice to melt, and the concentration of the solution will be thereby altered; salt must therefore dissolve until the original concentration is reached, and the heat of fusion of ice will be counteracted by the heat of solution of the salt. Changes of volume of the solid and liquid phases must also be taken into account; an alteration in the volume of these phases being compensated by condensation or evaporation. All four phases will therefore be involved in the change, and the final state of the system will be dependent on the amounts of the different phases present; the ultimate result of addition or withdrawal of heat or of change of pressure at the quadruple point will be one of the four univariant systems: ice—solution—vapour; salt—solution—vapour; ice—salt—vapour; ice—salt—solution. If the vapour phase disappear, there will be left the univariant system ice—salt—solution, and the temperature at which this system can exist will alter with the pressure. Since in this case the influence of pressure is comparatively slight, the temperature of the quadruple point will differ only slightly from that of the cryohydric point as determined under atmospheric pressure.

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[1] *Ber.*, 1877, **20**. 2223.

[2] *Sitz.-Ber. Wien. Akad.*, 1880, **81**. II. 1058.

[3] Guthrie, *Phil. Mag.*, 1875 [4], **49**. 206.

Freezing Mixtures.—Not only will the composition of a univariant system undergo change when the temperature is varied, but, conversely, if the *composition* of the system is caused to change, corresponding changes of temperature must ensue. Thus, if ice is added to the univariant system salt—solution—vapour, the ice must melt and the temperature fall; and if sufficient ice is added, the temperature of the cryohydric point must be at length reached, for it is only at this temperature that the four phases ice—salt—solution—vapour can coexist. Or, on the other hand, if salt is added to the system ice—solution—vapour, the concentration of the solution will increase, ice must melt, and the temperature must thereby fall; and this process also will go on until the cryohydric point is reached. In both cases ice melts and there is a change in the omposition of the solution; in the former case, salt will be eposited[1] because the solubility diminishes as the temperature alls; in the latter, salt will pass into solution. This process may be accompanied either by an evolution or, more generally, by absorption of heat; in the former case the effect of the addition of ice will be partially counteracted; in the latter case it will be augmented.

These principles are made use of in the preparation of *freezing mixtures.* The lowest temperature which can be reached by means of these (under atmospheric pressure) is the cryohydric point. This temperature-minimum is, however, not always attained in the preparation of a freezing mixture, and that for various reasons. The chief of these are radiation and the heat absorbed in cooling the solution produced. The lower the temperature falls, the more rapid does the radiation become; and the rate at which the temperature sinks decreases as the amount of solution increases. Both these factors counteract the effect of the latent heat of fusion and the heat of solution, so that a point is reached (which may lie considerably above the cryohydric point) at which the two opposing influences balance. The absorption of heat by the solution can be diminished by allowing the solution to drain off as fast as it is produced; and the effect of radiation can be partially annulled by increasing the rate of cooling. This can be done by the more intimate mixing of the components. Since, under atmospheric pressure, the temperature of the cryohydric point is constant, the cryohydrates are very valuable for the production of baths of constant low temperature.

2. *Partial Miscibility of the Fused Components.*

On passing to the study of the second class of systems of two components belonging to this group, namely, those in which the fused components are not miscible in all proporions, we find that the relationships are not quite so simple as in the case of silver nitrate and water. In the latter case, only one liquid phase was possible; in the cases now to be studied, two liquid phases can be formed, and there is a marked discontinuity in the solubility curve on passing from the cryohydric point to the melting point of the second (non-volatile) component.

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[1] If in the neighbourhood of the cryohydric point solution should be ccompanied by an evolution of heat, then as the solubility would in that se increase with fall of temperature, salt would pass into solution.

Paratoluidine dissolves in water, and the solubility increases as the temperature rises.[1] At 44·2°, however, paratoluidine in contact with water melts, and two liquid phases are formed, viz. a solution of water in fused paratoluidine and a solution of fused paratoluidine in water. We have, therefore, the phenomenon of *melting under the solvent.* This melting point will, of course, be lower than the melting point of the pure substance, because the solid is now in contact with a solution, and, as we have already seen, addition of a foreign substance lowers the melting point. Such cases of melting under the solvent are by no means rare, and a review of the relationships met with may, therefore, be undertaken here. As an example, there may be chosen the equilibrium between succinic nitrile, $C_2H_4(CN)_2$ and water, which has been fully studied by Schreinemakers.[2]

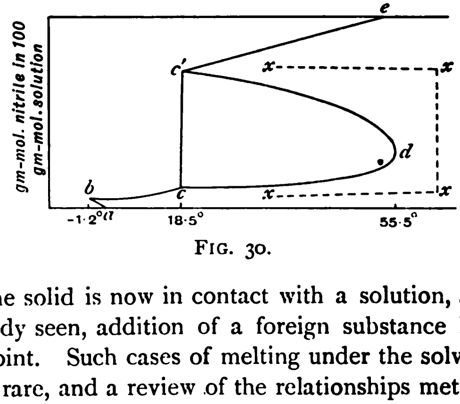

FIG. 30.

If to the system ice—water at 0° succinic nitrile is added, the temperature will fall; and continued addition of the nitrile will lead at last to the cryohydric point *b* (Fig. 30), at which solid nitrile, ice, solution, and vapour can coexist. The temperature of the cryohydric point is −1·2°, and the composition of the solution is 1·29 mol. of nitrile in 100 mol. of solution.

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[1] Walker, *Zeitschr. physikal. Chem.*, 1890, **5**. 193.

[2] *Zeitschr. physikal. Chem.*, 1897, **23**. 418.

om *a* to *b* the solid phase in contact with the solution is ice. the temperature be now raised so as to cause the disappear- ce of the ice, and the addition of nitrile be continued, the ncentration of the nitrile in the solution will increase as resented by the curve *bc*. At the point *c* (18·5°), when the ncentration of the nitrile in the solution has increased to 2·5 lecules per cent., the nitrile melts and two liquid phases are ned; the concentration of the nitrile in these two phases is en by the points *c* and *c′*. As there are now four phases sent, viz. solid nitrile, solution of fused nitrile in water, ution of water in fused nitrile, and vapour, the system is *ariant.* Since at this point the concentration, temperature, l pressure are completely defined, a further increase in the ount of nitrile can only cause a change in the relative ounts of the phases, *but no variation of the concentrations* of respective phases. As a matter of fact, continued addition nitrile will cause an increase in the amount of the liquid se containing excess of nitrile (*i.e.* the solution of water in ed nitrile), whereas the other liquid phase, the solution of ed nitrile in water, will gradually disappear. When it has npletely disappeared, the system will be represented by the int *c′*, where the molecular concentration of nitrile is now 75 cent., and again becomes univariant, the three phases being id nitrile, liquid phase containing excess of nitrile, and pour; and as the amount of the water is diminished the nperature of equilibrium rises, until at 54° the melting point the pure nitrile is reached.

Return now to the point *c*. At this point there exists the ariant system solid nitrile, two liquid phases, vapour. If at be added, the solid nitrile will disappear, and there will be t the univariant system, consisting of two liquid phases and pour. Such a system will exhibit relationships similar to se already studied in the previous chapter. As the temrature rises, the mutual solubility of the two fused comnents becomes greater, until at *d* (55·5°) the critical solution nperature is reached, and the fused components become iscible in all proportions.

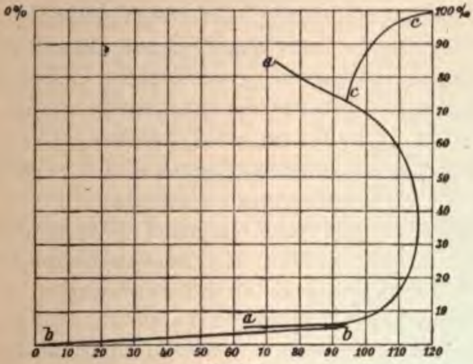
At all temperatures and concentrations lying to the right of the curve *abcdc'e* there can be only one liquid phase; in t field *cdc'* there are two liquid phases.

From the figure it will be easy to see what will be t result of bringing together succinic nitrile and water at differ temperatures and in different amounts. Since *b* is the low temperature at which liquid can exist in stable equilibrium w solid, ice and succinic nitrile can be mixed in any proporti at temperatures below *b* without undergoing change. Betw *b* and *c* succinic nitrile will be dissolved until the concentrat reaches the value on the curve *bc*, corresponding to the gi temperature. On adding the nitrile to water at temperat between *c* and *d*, it will dissolve until a concentration lying the curve *cd* is attained; at this point two liquid phases wil formed, and further addition of nitrile will cause the one li phase (that containing excess of nitrile) to increase, while other liquid phase will decrease, until it finally disappears there is only one liquid phase left, that containing exces nitrile. This can dissolve further quantities of the nitrile, the concentration will increase until the curve *c'e* is reac when the concentration will remain unchanged, and additio solid will merely increase the amount of the solid phase.

If a solution represented by any point in the field l below the curve *bcd* is heated to a temperature above *d*, critical solution temperature, then the concentration of nitrile can be increased to any desired amount without at time two liquid phases making their appearance; the sy can then be cooled down to a temperature represented by point between the curves *dc'e*. In this way it is possibl pass continuously from a solution containing excess of component to solutions containing excess of the othe represented by the dotted line *xxxx* (*v.* p. 98). At no p is there formation of two liquid phases.

Supersaturation.—Just as suspended transformation is ra met with in the passage from the solid to the liquid stat also it is found in the case of the melting of substances u the solvent that suspended fusion does not occur; but when the temperature of the invariant point is reache which, therefore, the formation of two liquid layers is possi these two liquid layers, as a matter of fact, make their appearance. Suspended transformation can, however, take place from the side of the liquid phase, just as water or other liquid can be cooled below the normal freezing point without solidification occurring. The question, therefore, arises as to the relative solubilities of the solid and the supercooled liquid at the same temperature.

The answer to this question can at once be given from what we have already learned (p. 111), if we recollect that at temperatures below the point of fusion under the solvent, the solid form, at temperatures above that point, the liquid form,



a, a = liquid }
b, b, and c, c = solid } *Benzoic acid.*

FIG. 31.

is the more stable; at this temperature, therefore, the relative stability of the solid and liquid forms changes. Since, as we have already seen, the less stable form has the greater solubility, it follows that the supercooled liquid, being the less stable form, must have the greater solubility. This was first proved experimentally by Alexejeff[1] in the case of benzoic acid and water, the solubility curves for which are given in Fig. 31. As an be seen from the figure, the prolongation of the curve for uid—liquid, which represents the solubility of the supercooled uid benzoic acid, lies above that for the solubility of the solid benzoic acid in water; the solution saturated with respect to the supercooled liquid is therefore supersaturated with respect to the solid form. A similar behaviour has been found in the case of other substances.[1]

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[1] *Wied. Annalen*, 1886, **28**. 328. Cf. Ostwald, *Lehrbuch*, II. 2. 872.

Pressure-Temperature Diagram.—Having considered the changes which occur in the concentration of the components in a solution with the temperature, we may conclude the discussion of the equilibrium between a salt and water by studying the variation of the vapour pressure.

Since in systems of two components the two phases, solution and vapour, constitute a bivariant system, the vapour pressure is undefined, and may have different values at the same temperature, depending on the concentration. In order that there may be for each temperature a definite corresponding pressure of the vapour, a third phase must be present. This condition is satisfied by the system solid—liquid (solution) —vapour; that is, by the saturated solution (p. 106). In the case of a saturated solution, therefore, the pressure of the vapour at any given temperature is constant.

Vapour Pressure of Solid—Solution—Vapour.—It has long been known that the addition of a non-volatile solid to a liquid in which it is soluble lowers the vapour pressure of the solvent; and the diminution of the pressure is approximately proportional to the amount of substance dissolved (Law of Babo). The vapour-pressure curve, therefore, of a solution of a salt in water must lie below that for pure water. Further, in the case of a pure liquid, the vaporization curve is a function only of the temperature (p. 61), whereas, in the case of a solution, the pressure varies both with the temperature and the *concentration*. These two factors, however, act in opposite directions; for although the vapour pressure in all cases increases as the temperature rises, increase of concentration, as we have seen, lowers the vapour pressure. Again, since the concentration itself varies with the temperature, two cases have to be considered, viz. where the concentration increases with rise of temperature, and where the concentration diminishes with rise of temperature.

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[1] Walker, *Zeitschr. physikal. Chem.*, 1890, **5**. 193. Schreinemakers, *ibid.*, 1897, **23**. 417. Roozeboom, *Rec. trav. chim. Pays-Bays*, 1889, **8**. 257. Bruner, *Zeitschr. physikal. Chem.* 1897, **23**. 542.

The relations which are found here will be best understood with the help of Fig. 32.[1] In this figure, OB represents the sublimation curve of ice, and BC the vaporization curve of water; the curve for the solution must lie below this, and must cut the sublimation curve of ice at some temperature below the melting point. The point of intersection A is the cryohydric point. If the solubility increases with rise of temperature, the increase of the vapour pressure due to the latter will be partially annulled. Since at first the effect of increase of temperature more than counteracts the depressing action of increase of concentration, the vapour pressure will increase on raising the temperature above the cryohydric point. If the elevation of temperature is continued, however, to the melting point of the salt, the effect of increasing concentration makes itself more and more felt, so that the vapour-pressure curve of the solution falls more and more below that of the pure liquid, and the pressure will ultimately become equal to that of the pure salt; that is to say, practically equal to zero. The curve will therefore be of the general form AMF shown in Fig. 32. If the solubility should diminish with rise of temperature, the two factors, temperature and concentration, will act in the same direction, and the vapour-pressure curve will rise relatively more rapid than that of the pure liquid; since, however, the pure salt is ultimately obtained, the vapour-pressure curve must in this case also finally approach the value zero.

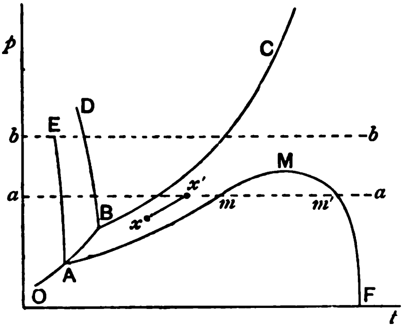

FIG. 32.

Other Univariant Systems.—Besides the univariant system salt—solution—vapour already considered, three others are possible, viz. ice—solution—vapour, ice—salt—solution, and ice—salt—vapour.

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[1] Van't Hoff, *Lectures on Theoretical Chemistry*, I. p. 42. Ostwald, *Lehrbuch*, II. 2. 824.

The fusion point of a substance is lowered, as we have seen, by the addition of a foreign substance, and the depression is all the greater the larger the quantity of substance added. The vapour pressure of the water, also, is lowered by the solution in it of other substances, so that the vapour pressure of the system ice—solution—vapour must decrease as the temperature falls from the fusion point of ice to the cryohydric point. This curve is represented by BA (Fig. 32), and is coincident with the sublimation curve of ice.

This, at first sight, strange fact will be readily understood when we consider that since ice and solution are together in equilibrium with the same vapour, they must have the same vapour pressure. For suppose at any given temperature equilibrium to have been established in the system ice—solution—vapour, removal of the ice will not alter this equilibrium. Suppose, now, the ice and the solution placed under a bell-jar so that they have a common vapour, but are not themselves in contact; then, if they do not have the same vapour pressure, distillation must take place and the solution will become more dilute or more concentrated. Since, at the completion of this process, the ice and solution are now in equilibrium when they are not in contact, they must also be in equilibrium when they are in contact (p. 30). But if distillation has taken place the concentration of the solution must have altered, so that the ice will now be in equilibrium with a solution of a different concentration from before. But according to the Phase Rule ice cannot at one and the same temperature be in equilibrium with two solutions of different concentration, for the system ice—solution—vapour is univariant, and at any given temperature, therefore, not only the pressure but also the *concentration of the components in the solution must be constant.* Distillation could not, therefore, take place from the ice to the solution or *vice versâ*; that is to say, the solution and the ice must have the same vapour pressure—the sublimation pressure of ice. The reason of the coincidence is the non-volatility of the salt: had salt a measurable vapour pressure itself, the sublimation rve of ice and the curve for ice—solution—vapour would no nger fall together.

The curve AO represents the pressures of the system ice—lt—vapour. This curve will also be coincident with the ublimation curve of ice, on account of the non-volatility of the alt.

The equilibria of the fourth univariant system ice—salt—solution are represented by AE. Since this is a condensed system, the effect of a small change of temperature will be to cause a large change of pressure, as in the case of the fusion point of a pure substance. The direction of this curve will depend on whether there is an increase or diminution of volume on solidification; but the effect in any given case can be predicted with the help of the theorem of Le Chatelier.

Since the cryohydric point is a quadruple point in a two-component system, it represents an invariant system. The condition of the system is, therefore, completely defined; the four phases, ice, salt, solution, vapour, can co-exist only when the temperature, pressure, and concentration of the solution have constant and definite values. Addition or withdrawal of heat, therefore, can cause no alteration of the condition of the system except a variation of the relative amounts of the phases. Addition of heat at constant volume will ultimately lead to the system salt—solution—vapour or the system ice—solution—vapour, according as ice or salt disappears first. This is readily apparent from the diagram (Fig. 32), for the systems ice—salt—solution and ice—salt—vapour can exist only at temperatures below the cryohydric point (provided the curve for ice—salt—solution slopes towards the pressure axis).

Bivariant Systems.—Besides the univariant systems already discussed, various bivariant systems are possible, the conditions for the existence of which are represented by the different areas of Fig. 32. They are as follows:—

Area.	*System.*
OAMF . . .	Salt—vapour.
CBAMF . . .	Solution—vapour; salt—solution.
EABD . . .	Salt—solution; ice—solution.
EAO . . .	Ice—salt.

Deliquescence.—As is evident from Fig. 32, salt can exist in contact with water vapour at pressures under those represented by OAMF. If, however, the pressure of the vapour is increased until it reaches a value lying on this curve at temperatures above the cryohydric point, solution will be formed; for the curve AMF represents the equilibria between salt—solution—vapour. From this, therefore, it is clear that if the pressure of the aqueous vapour in the atmosphere is greater than that of the saturated solution of a salt, that salt will, on being placed in the air, form a solution; it will *deliquesce.*

Separation of Salt on Evaporation.—With the help of Fig. 32 it is possible to state in a general manner whether or not salt will be deposited when a solution is evaporated under a constant pressure.[1]

The curve AMF (Fig. 32) is the vapour-pressure curve of the saturated solutions of the salt, *i.e.* it represents, as we have seen, the maximum vapour pressure at which salt can exist in contact with solution and vapour. The dotted line *aa* represents atmospheric pressure. If, now, an unsaturated solution, the composition of which is represented by the point x, is heated in an open vessel, the temperature will rise, and the vapour pressure of the solution will increase. The system will, therefore, pass along a line represented diagrammatically by xx'. At the point x' the vapour pressure of the system becomes equal to 1 atm.; and as the vessel is open to the air, the pressure cannot further rise; the solution boils. If the heating is continued, water passes off, the concentration increases, and the boiling point rises. The system will therefore pass along the line $x'm$, until at the point m solid salt separates out (provided supersaturation is excluded). The system is now univariant, and continued heating will no longer cause an alteration of the concentration; as water passes off, solid salt will be deposited, and the solution will evaporate to dryness.

If, however, the atmospheric pressure is represented not by *aa* but by *bb*, then, as Fig. 32 shows, the maximum vapour

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[1] Ostwald, *Principles of Inorganic Chemistry*, translated by A. Findlay, p. 447 (Macmillan, 1902); Skirrow and Calvert, *Zeitschr. physikal. Chem.*, 1901, **37**. 217.

: of the system salt—solution—vapour never reaches sure of 1 atm. Further, since the curve *bb* lies in the the bivariant system solution—vapour there can at no : a separation of the solid form; for the system solid— —vapour can exist only along the curve AMF.

evaporating the solution of a salt in an open vessel, e, salt can be deposited only if at some temperature ssure of the saturated solution is equal to the atmo-pressure. This is found to be the case with most salts. case of aqueous solutions of sodium and potassium de, however, the vapour pressure of the saturated never reaches the value of 1 atm., and on evaporating utions, therefore, in an open vessel, there is no separa-he solid. Only a homogeneous fused mass is obtained. ever, the evaporation be carried out under a pressure s lower than the maximum pressure of the saturated , separation of the solid substance will be possible.

eral Summary.—The systems which have been dis-n the present chapter contained water as one of their ents, and an anhydrous salt as the other. It will, , be clear that the relationships which were found in of these will be found also in other cases where it is on of the equilibria between two components, which ze out in the pure state, and only one of which possesses urable vapour pressure. A similar behaviour will, for , be found in the case of many pairs of organic sub- and in all cases the equilibria will be represented by m of the general appearance of Fig. 29 or Fig. 30. to say: Starting from the fusion point of component I., em will pass, by progressive addition of component II., ns of lower temperature, until at last the cryohydric or point is reached. On further addition of component system will pass to regions of higher temperature, the ase now being component II. If the fused components ible with one another in all proportions a continuous ill be obtained leading up to the point of fusion of ent II. Slight changes of direction, it is true, due to in the crystalline form, may be found along this curve, but throughout its whole course there will be but one liquid phase. If, on the other hand, the fused components are not miscible in all proportions, then the second curve will exhibit a marked discontinuity, and two liquid phases will make their appearance.

CHAPTER VIII

SOLUTIONS OF SOLIDS IN LIQUIDS, ONLY ONE OF THE COMPONENTS BEING VOLATILE

B.—Hydrated Salt and Water.

In the preceding chapter we discussed the behaviour of systems formed of two components, only one of which was volatile, in those cases where the two components separated from solution in the pure state. In the present chapter we shall consider those systems in which combination between the components can occur with the formation of definite compounds; such as are found in the case of crystalline salt hydrates. Since a not inconsiderable amount of study has been devoted to the systems formed by hydrated salts and water, systems which are of great chemical interest and importance, the behaviour of these will first call for discussion in some detail, and it will be found later that the relationships which exist in such systems appear also in a large number of other two-component systems.

The systems belonging to this group may be divided into two classes according as the compounds formed possess a definite melting point, *i.e.* form a liquid phase of the same composition, or do not do so. We shall consider the latter first.

1. *The Compounds formed do not have a Definite Melting Point.*

Concentration-Temperature Diagram.—In the case of alts which can form crystalline hydrates, the temperature-oncentration diagram, representing the equilibria of the different possible systems, must necessarily be somewhat complicated than where no such combination of the compc occurs. For, as has already been pointed out, each subs has its own solubility curve; and there will therefore many solubility curves as there are solid phases possib *curve for each particular solid phase being continuous so l it remains unchanged in contact with the solution.* As ample of the relationships met with in such cases, we sha of all consider the systems formed of sodium sulphat water.

Sodium Sulphate and Water.—At the ordinary ter tures, sodium sulphate crystallises from water with ten mol of water of crystalli forming Glauber's salt determining the solubi this salt in water, it is that the solubility inc as the temperature rise values of the solubilit presented graphically l curve AC (Fig. 33), given in the following table.[1] The numbers denote gra sodium sulphate, calculated as anhydrous salt, dissolv 100 grams of water.

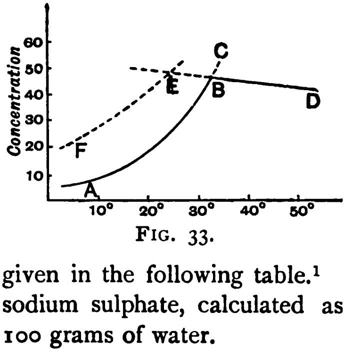

FIG. 33.

SOLUBILITY OF $Na_2SO_4,10H_2O$.

Temperature.	Solubility.
0°	5·02
10°	9·00
15°	13·20
18°	16·80
20°	19·40
25°	28·00
30°	40·00
33°	50·76
34°	55·00

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[1] *Vide* Loewel, *Annales chim. phys.*, 1857 [3], **49**. 32. Cf. Löw *Zeitschr. physikal. Chem.*, 1895, **18**. 82.

On continuing the investigation at higher temperatures, it was found that the solubility no longer increased, but *decreased with rise of temperature.* At the same time, it was observed that the solid phase was now different from that in contact with the solution at temperatures below 33°; for whereas in the latter case the solid phase was sodium sulphate decahydrate, at temperatures above 33° the solid phase was the anhydrous salt. The course of the solubility curve of anhydrous sodium sulphate is shown by BD, and the values of the solubility are given in the following table :—[1]

SOLUBILITY OF ANHYDROUS SODIUM SULPHATE.

Temperature.	Solubility.
18°	53·25
20°	52·76
25°	51·53
30°	50·37
33°	49·71
34°	49·53
36°	49·27
40·15°	48·78
50·40°	46·82

As is evident from the figure, the solubility curve which is obtained when anhydrous sodium sulphate is present as the solid phase, cuts the curve representing the solubility of the decahydrate, at a temperature of about 33°.

If a solution of sodium sulphate which has been saturated at a temperature of about 34° be cooled down to a temperature below 17°, while care is taken that the solution is protected against access of particles of Glauber's salt, crystals of a second hydrate of sodium sulphate, having the composition $Na_2SO_4,7H_2O$, separate out. On determining the composition of the solutions in equilibrium with this hydrate at different temperatures, the following values were obtained, these values being represented by the curve FE (Fig. 33) :—

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[1] Loewel, *loc. cit.* Gay-Lussac, *Annales chim. phys.*, 1819, **11**. 296. r the solubility at higher temperatures, see Tilden and Shenstone, *Phil. ans.*, 1884, **175**. 23. Étard, *Annales chim. phys.*, 1894 [7], 2. 548.

SOLUBILITY OF $Na_2SO_4,7H_2O$.

Temperature.	Solubility.
0°	19·62
10°	30·49
15°	37·43
18°	41·63
20°	44·73
25°	52·94
26°	54·97

Since, as has already been stated, each solid substa its own solubility curve, there are three separate curve considered in the case of sodium sulphate and water. two curves cut, the solution must be saturated with re two solid phases; at the point B, therefore, the point section of the solubility curve of anhydrous sodium with that of the decahydrate, the solution must be s with respect to these two solid substances. But a system components existing in four phases, anhydrous salt—h salt—solution—vapour, is invariant; and this invariabi remain even if only three phases are present, provid one of the factors, pressure, temperature, or concentr components retains a constant value. This is the cas solubilities are determined in open vessels; the pre then equal to atmospheric pressure. Under these circum then, the system, anhydrous sodium sulphate—decahy solution, will possess no degree of freedom, and ca therefore, only at one definite temperature and when t tion has a certain definite composition. The temper this point is 32·482° on a mercury thermometer, or 32· the hydrogen thermometer.[1]

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[1] Richards, *Zeitschr. physikal. Chem.*, 1898, **26**. 690; Rich Wells, *ibid.*, 1903, **43**. 465. This temperature is not quite the that of the *quadruple point* anhydrous salt—hydrated salt—solution because the latter is the temperature at which the system is pressure of its own vapour. Since, however, the influence of pr the solubility is very slight (p. 105), the position of the two p not be greatly different. The quadruple point was found

Suspended Transformation.—Although it is possible for the anhydrous salt to make its appearance at the temperature of the quadruple point, it will not necessarily do so; and it is therefore possible to follow the solubility curve of sodium sulphate decahydrate to a higher temperature. Since, however, the solubility of the decahydrate at temperatures above the quadruple point is greater than that of the anhydrous salt, the solution which is *saturated* with respect to the former will be *supersaturated* with respect to the latter. On bringing a small quantity of the anhydrous salt in contact with the solution, therefore, anhydrous salt will be deposited; and all the hydrated salt present will ultimately undergo conversion into the anhydrous salt, through the medium of the solution. In this case, as in all cases, the solid phase, which is the most stable at the temperature of the experiment, has at that temperature the least solubility.

Similarly, the solubility curve of anhydrous sodium sulphate has been followed to temperatures below 32·5°. Below this temperature, however, the solubility of this salt is greater than that of the decahydrate, and the saturated solution of the anhydrous salt will therefore be supersaturated for the decahydrate, and will deposit this salt if a "nucleus" is added to the solution. From this we see that at temperatures above 32·5° the anhydrous salt is the stable form, while the decahydrate is unstable (or metastable); at temperatures below 32·5° the decahydrate is stable. This temperature, therefore, is the *transition temperature* for decahydrate and anhydrous salt.

From Fig. 33 we see further that the solubility curve of the anhydrous salt (which at all temperatures below 32·5° is metastable) is cut by the solubility curve of the heptahydrate; and this point of intersection (at a temperature of 24·2°) must be the *transition point* for heptahydrate and anhydrous salt. Since at all temperatures the solubility of the heptahydrate is greater than that of the decahydrate, the former hydrate must be metastable with respect to the latter; so that throughout its whole course the solubility curve of the heptahydrate

(*Zeitschr. physikal. Chem.*, 1894, 14. 90) to be 32·6° and 30·8 mm. of mercury.

represents only metastable equilibria. Sodium sulphate, therefore, forms only one stable hydrate, the decahydrate.

The solubility relations of sodium sulphate illustrate very clearly the importance of the solid phase for the definition of saturation and supersaturation. Since the solubility curve of the anhydrous salt has been followed backwards to a temperature of about 18°, it is readily seen, from Fig. 33, that at a temperature of, say, 20° three different *saturated* solutions of sodium sulphate are possible, according as the anhydrous salt, the heptahydrate or the decahydrate, is present as the solid phase. Two of these solutions, however, would be metastable and *supersaturated with respect to the decahydrate.*

Further, the behaviour of sodium sulphate and water furnishes a very good example of the fact that a "break" in the solubility curve occurs when, and only when, the solid phase undergoes change. So long as the decahydrate, for example, remained unaltered in contact with the solution, the solubility curve was continuous; but when the anhydrous salt appeared in the solid phase, a distinct change in the direction of the solubility curve was observed.

Dehydration by Means of Anhydrous Sodium Sulphate.—The change in the relative stability of sodium sulphate decahydrate and anhydrous salt in presence of water at a temperature of 32·5° explains why the latter salt cannot be employed for dehydration purposes at temperatures above the transition point. The dehydrating action of the anhydrous salt depends on the formation of the decahydrate; but since at temperatures above 33° the latter is unstable, and cannot be formed in presence of the anhydrous salt, this salt cannot, of course, effect a dehydration above that temperature.

Pressure-Temperature Diagram.—The consideration of the pressure-temperature relations of the two components, sodiun sulphate and water, must include not only the vapour pressur of the saturated solutions, but also that of the crystallin hydrates. The vapour pressures of salt hydrates have alread been treated in a general manner (Chap. V.), so that it is onl necessary here to point out the connection between the tw classes of systems.

In most cases the vapour pressure of a salt hydrate, *i.e.* the vapour pressure of the system hydrate—anhydrous salt (or lower hydrate)—vapour, is at all temperatures lower than that of the system anhydrous salt (or lower hydrate)—solution—vapour. This, however, is not a necessity; and cases are known where the vapour pressure of the former system is, under certain circumstances, equal to or higher than that of the latter. An example of this is found in sodium sulphate decahydrate.

On heating $Na_2SO_4,10H_2O$, a point is reached at which the dissociation pressure into anhydrous salt and water vapour becomes equal to the vapour pressure of the saturated solution of the anhydrous salt, as is apparent from the following measurements;[1] the differences in pressure being expressed in millimetres of a particular oil.

Temperature:	29·0°	30·83°	31·79°	32·09°	32·35°	32·6°
Difference of pressure:	23·8	10·8	5·6	3·6	1·6	0

At 32·6°, therefore, the vapour pressures of the two systems

$Na_2SO_4,10H_2O$—Na_2SO_4—vapour
Na_2SO_4—solution—vapour

are equal; at this temperature the four phases, $Na_2SO_4,10H_2O$; Na_2SO_4; solution; vapour, can coexist. From this it is evident that when sodium sulphate decahydrate is heated to 32·6°, the two new phases anhydrous salt and solution will be formed (suspended transformation being supposed excluded), and the hydrate will appear to undergo *partial fusion*; and during the process of "melting" the vapour pressure and temperature will remain constant.[2] This is, however, no true melting point; for the composition of the liquid phase is not the same as that of the solid. As has already been pointed out (p. 135), we are dealing here with the *transition point* of the decahydrate and anhydrous salt, *i.e.* with the reaction $Na_2SO_4,10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$.

Since at the point of partial fusion of the decahydrate four

[1] Van't Hoff and van Deventer, *Zeitschr. physikal. Chem.*, 1887, **1**. 185. *C.f.* Cohen, *ibid.*, 1894, **14**. 88.

[2] Debray, *Compt. rend.*, 1868, **66**. 194.

phases can coexist, the point is a quadruple point in a two-component system, and the system at this point is therefore invariant. The temperature of this point is therefore perfectly definite, and on this account the proposal has been made to adopt this as a fixed point in thermometry.[1] The temperature is, of course, practically the same as that at which the two solubility curves intersect (p. 110).

The vapour pressure of the different systems of sodium sulphate and water can best be studied with the help of the diagram in Fig. 34.[2] The curve ABCD represents the vapour-pressure curve of the saturated solution of anhydrous sodium sulphate. GC is the pressure curve of decahydrate + anhydrous salt, which, as we have seen, cuts the curve ABCD at the transition temperature, 32·6°. Since at this point the solution is saturated with respect to both the anhydrous salt and the decahydrate, the vapour-pressure curve of the saturated solution of the latter must also pass through the point C.[3] As at temperatures below this point the solubility of the decahydrate is less than that of the anhydrous salt, the vapour pressure of the solution will, in accordance with Babo's law (p. 124), be higher than that of the solution of the anhydrous salt; which was also found experimentally to be the case (curve HC).

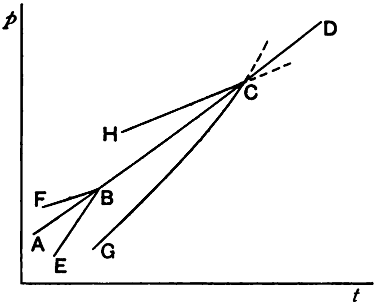

FIG. 34.

In connection with the vapour pressure of the saturated solutions of the anhydrous salt and the decahydrate, attention must be drawn to a conspicuous deviation from what was found to hold in the case of one-component systems in which a vapour phase was present (p. 29). There, it was seen that the vapour pressure of the more stable system was always *lower* than that of the less stable; in the present case, however, we find that this is no longer so. We have already learned that at temperatures below 32·5° the system decahydrate—solution—vapour is more stable than the system anhydrous salt—solution—vapour; but the vapour pressure of the latter system is, as has just been stated, lower than that of the former. At temperatures above the transition point the vapour pressure of the saturated solution of the decahydrate will be lower than that of the saturated solution of the anhydrous salt.

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[1] Richards, *Zeitschr. physikal. Chem.*, 1898, **26.** 690. A number of other salt hydrates, having transition-points ranging from 20° to 78°, which might be used for the same purpose, have been given by Richards and Churchill, *ibid.*, 1899, **28.** 313.

[2] Van't Hoff, *Lectures on Physical Chemistry*, I. p. 67.

[3] Cohen, *Zeitschr. physikal. Chem.*, 1894, **14.** 90.

This behaviour depends on the fact that the less stable form is the more soluble, and that the diminution of the vapour pressure increases with the amount of salt dissolved.

With regard to sodium sulphate heptahydrate the same considerations will hold as in the case of the decahydrate. Since at 24° the four phases heptahydrate, anhydrous salt, solution, vapour can coexist, the vapour-pressure curves of the systems hydrate—anhydrous salt—vapour (curve EB) and hydrate—solution—vapour (curve FB) must cut the pressure curve of the saturated solution of the anhydrous salt at the above temperature, as represented in Fig. 34 by the point B. This constitutes, therefore, a second quadruple point, which is, however, metastable.

From the diagram it is also evident that the dissociation pressure of the heptahydrate is higher than that of the decahydrate, although it contains less water of crystallization. The system heptahydrate—anhydrous salt—vapour must be metastable with respect to the system decahydrate—anhydrous salt—vapour, and will pass into the latter.[1] Whether or not there is a temperature at which the vapour-pressure curves of the two systems intersect, and below which the heptahydrate becomes the more stable form, is not known.

In the case of sodium sulphate there is only one stable hydrate. Other salts are known which exhibit a similar behaviour; and we shall therefore expect that the solubility relationships will be represented by a diagram similar to that for sodium sulphate. A considerable number of such cases have, indeed, been found,[1] and in some cases there is more than one metastable hydrate. This is found, for example, in the case of nickel iodate,[2] the solubility curves for which are given in Fig. 35. As can be seen from the figure, suspended transformation occurs, the solubility curves having in some cases been followed to a considerable distance beyond the transition point. One of the most brilliant examples, however, of suspended transformation in the case of salt hydrates, and the sluggish transition from the less stable to the more stable form, is found in the case of the hydrates of calcium chromate.[3]

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[1] Ziz, *Schweigger's Journal*, 1815, 15. 166. See Ostwald, *Lehrbuch*, II. 2. 717.

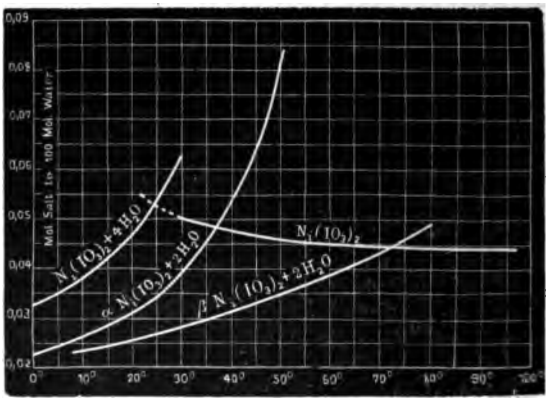

FIG. 35.

In the preceding cases, the dissociation-pressure curve of the hydrated salt cuts the vapour-pressure curve of the saturated solution of the anhydrous salt. It can, however, happen that

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[1] See, for example, the solubility determinations published in *Wissenschaftliche Abhandl. der physikalisch-technischen Reichsanstalt*, Vol. III., or in the *Berichte*, for the years 1897–1901.

[2] Meusser, *Ber.*, 1901, **34.** 2440.

[3] Mylius and von Wrochem, *Ber.*, 1900, **33.** 3693.

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dissociation-pressure curve of one hydrate cuts the (solubility) 're, not of the anhydrous salt, but of a lower hydrate; in this : there will be more than one stable hydrate, each having a le solubility curve; and these curves will intersect at the perature of the transition point. Various examples of this ıviour are known, and we choose for illustration the soluy relationships of barium acetate and its hydrates, which : been recently determined[1] (Fig. 36).

At temperatures above 0°, barium acetate can form two le hydrates, a trihydrate and a monohydrate. The solu-

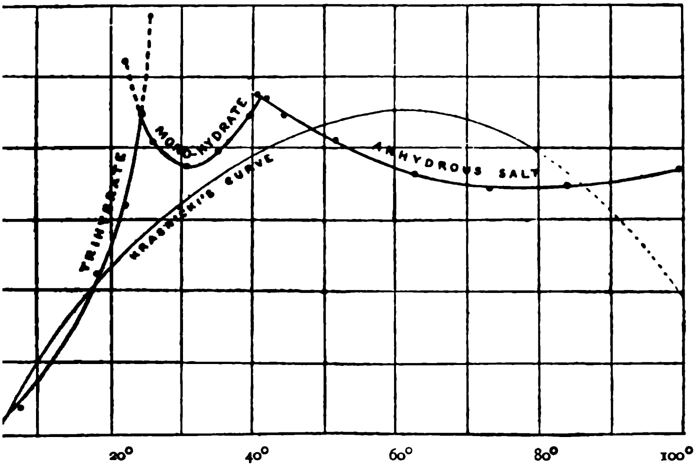

FIG. 36.

ty of the trihydrate increases very rapidly with rise of temature, and has been determined up to 26·1°. At temperatures ›ve 24·7°, however, the trihydrate is metastable with respect the monohydrate; for at this temperature the solubility ve of the latter hydrate cuts that of the former. This is, refore, the transition temperature for the trihydrate and ıohydrate. The solubility curve of the monohydrate sucds that of the trihydrate, and exhibits a conspicuous ınt of minimum solubility at about 30°. Below 24·7° the monohydrate is the less stable hydrate, but its solubili been determined to a temperature of 22°. At 41° the sol curve of the monohydrate intersects that of the anhydro and this is therefore the transition temperature for the hydrate and anhydrous salt. Above this temperatu anhydrous salt is the stable solid phase. Its solubility also passes through a minimum.

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[1] Walker and Fyffe, *Jour. Chem. Soc.*, 1903, **83**. 180.

The diagram of solubilities of barium acetate nc illustrates the way in which the solubility curves of the d stable hydrates of a salt succeed one another, but it has interest and importance from another point of view. 36 there is also shown a faintly drawn curve which is con throughout its whole course. This curve represents th bility of barium acetate as determined by Krasnicki.[1] however, three different solid phases can exist und conditions of experiment, it is evident, from what has been stated (p. 109), that the different equilibria between acetate and water could not be represented by one *con* curve.

Another point which these experiments illustrate anc it is of the highest importance to bear in mind is, making determinations of the solubility of salts whi capable of forming hydrates, it is not only neces determine the composition of the solution, but *it is* *importance to determine the composition of the solid p contact with it.* In view of the fact, also, that the equilibrium is in many cases established with com slowness, it is necessary to confirm the point of equil either by approaching it from higher as well as fron temperatures, or by actually determining the rate wit the condition of equilibrium is attained. This can be plished by actual weighing of the dissolved salt or b minations of the density of the solution, as well as b methods.

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[1] *Monatshefte*, 1887, S. 601.

2. *The Compounds formed have a Definite Melting Point.*

In the cases which have just been considered we saw that the salt hydrates on being heated did not undergo complete fusion, but that a solid was deposited consisting of a lower hydrate or of the anhydrous salt. It has, however, been long known that certain crystalline salt hydrates (*e.g.* sodium thiosulphate, $Na_2S_2O_3,5H_2O$, sodium acetate, $NaC_2H_3O_2,3H_2O$) melt completely in their water of crystallization, and yield a liquid of the *same composition* as the crystalline salt. In the case of sodium thiosulphate pentahydrate the temperature of liquefaction is 56°; in the case of sodium acetate trihydrate, 58°. These two salts, therefore, have a definite melting point. For the purpose of studying the behaviour of such salt hydrates, we shall choose not the cases which have just been mentioned, but two others which have been more fully studied, viz. the hydrates of calcium chloride and of ferric chloride.

Solubility Curve of Calcium Chloride Hexahydrate.[1]—Although calcium chloride forms several hydrates, each of which possesses its own solubility, it is nevertheless the solubility curve of the hexahydrate which will chiefly interest us at present, and we shall therefore first discuss that curve by itself.

The solubility of this salt has been determined from the cryohydric point, which lies at about −55°, up to the melting point of the salt.[2] The solubility increases with rise of temperature, as is shown by the figures in the following table, and by the (diagrammatic) curve AB in Fig. 37. In the table, the numbers under the heading "solubility" denote the number of grams of $CaCl_2$ dissolved in 100 grams

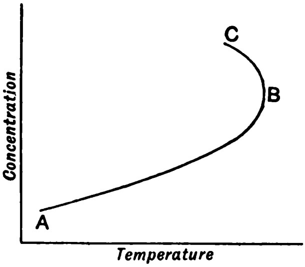

FIG. 37.

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[1] The equilibria between calcium chloride and water have been most completely studied by Roozeboom (*Zeitschr. physikal. Chem.*, 1889, 4. 31).

[2] Hammerl, *Sitzungsber. Wien. Akad*, 2^{te} Abteil, 1878, 78. 59. Roozeboom, *Zeitschr. physikal. Chem.*, 1889, 4. 31.

of water; those under the heading "composition," the number of gram-molecules of water in the solution to one gram-molecule of $CaCl_2$.

SOLUBILITY OF CALCIUM CHLORIDE HEXAHYDRATE.

Temperature.	Solubility.	Composition.
−55°	42·5	14·5
−25°	50·0	12·3
−10°	55·0	11·2
0°	59·5	10·37
10°	65·0	9·49
20°	74·5	8·28
25°	82·0	7·52
28·5°	90·5	6·81
29·5°	95·5	6·46
30·2°	102·7	6·00
29·6°	109·0	5·70
29·2°	112·8	5·41

So far as the first portion of the curve is concerned, it resembles the most general type of solubility curve. In the present case the solubility is so great and increases so rapidly with rise of temperature, that a point is reached at which the water of crystallization of the salt is sufficient for its complete solution. This temperature is 30·2°; and since the composition of the solution is the same as that of the solid salt, viz. 1 mol. of $CaCl_2$ to 6 mols. of water, this temperature must be the melting point of the hexahydrate. At this point the hydrate will fuse or the solution will solidify without change of temperature and without change of composition.

But the solubility curve of calcium chloride hexahydrate differs markedly from the other solubility curves hitherto considered in that it possesses a *retroflex portion*, represented in the figure by BC. As is evident from the figure, therefore, calcium chloride hexahydrate exhibits the peculiar and, as it was at first thought, impossible behaviour that it can be in equilibrium at one and the same temperature with two different solutions, one of which contains more, the other less, water than the solid hydrate; for it must be remembered that hroughout the whole course of the curve ABC the solid phase present in equilibrium with the solution is the hexahydrate.

Such a behaviour, however, on the part of calcium chloride hexahydrate will appear less strange if one reflects that the melting point of the hydrate will, like the melting point of other substances, be lowered by the addition of a second substance. If, therefore, water is added to the hydrate at its melting point, the temperature at which the solid hydrate will be in equilibrium with the liquid phase (solution) will be lowered; or if, on the other hand, anhydrous calcium chloride is added to the hydrate at its melting point (or what is the same thing, if water is removed from the solution), the temperature at which the hydrate will be in equilibrium with the liquid will also be lowered; *i.e.* the hydrate will melt at a lower temperature. In the former case we have the hydrate in equilibrium with a solution containing more water, in the latter case with a solution containing less water than is contained in the hydrate itself.

It has already been stated (p. 109) that the solubility curve (in general, the equilibrium curve) is continuous so long as the solid phase remains unchanged; and we shall therefore expect that the curve ABC will be continuous. Formerly, however, it was considered by some that the curve was not continuous, but that the melting point is the point of intersection of two curves, a solubility curve and a fusion curve. Although the earlier solubility determinations were insufficient to decide this point conclusively, more recent investigation has proved beyond doubt that the curve is continuous and exhibits no break.[1]

Although in taking up the discussion of the equilibria between calcium chloride and water, it was desired especially to call attention to the form of the solubility curve in the case of salt hydrates possessing a definite melting point, nevertheless, for the sake of completeness, brief mention may be made of the other systems which these two components can form.

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[1] Lidbury, *Zeitschr. physikal. Chem.*, 1902, **39**. 453. The curvature at he melting point is all the greater the more the compound is dissociated nto its components in the liquid state. If the compound is *completely undissociated*, even in the vapour phase, the two branches of the curve will *ntersect*. The smaller the degree of dissociation, therefore, the sharper will be the bend. (See Stortenbeker, *Zeitschr. physikal. Chem.*, 1892, **10**. 94.)

Besides the hexahydrate, the solubility curve of which has

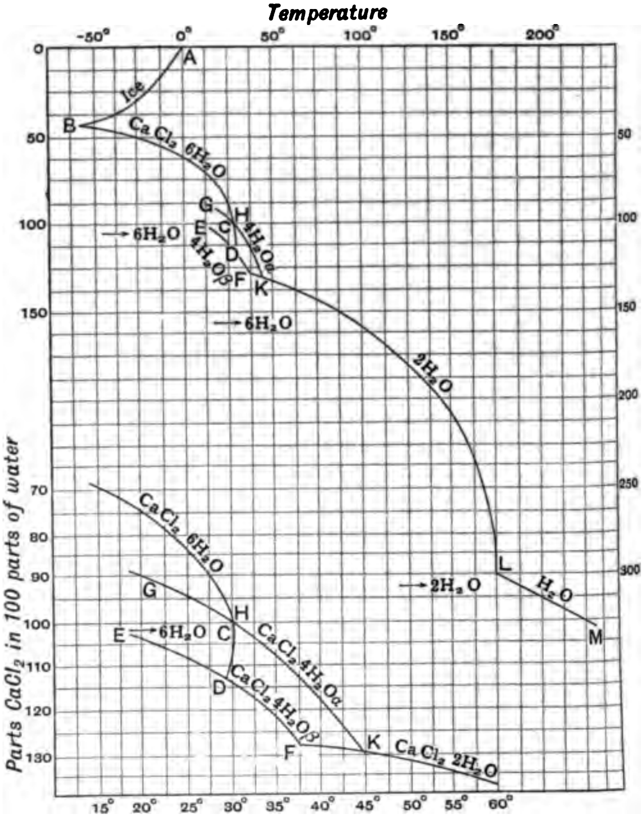

FIG. 38.

already been described, calcium chloride can also crystallize in two different forms, each of which contains four molecules of water of crystallization; these are distinguished as α-tetrahydrate, and β-tetrahydrate. Two other hydrates are also own, viz. a dihydrate and a monohydrate. The solubility rves of these different hydrates are given in Fig. 38.

On following the solubility curve of the hexahydrate from e ordinary temperature upwards, it is seen that at a tempera-re of 29·8° represented by the point H, it cuts the solubility rve of the α-tetrahydrate. This point is therefore a quad-ple point at which the four phases hexahydrate, α-tetrahydrate, lution, and vapour can coexist. It is also the transition int for these two hydrates. Since, at temperatures above ·8°, the α-tetrahydrate is the stable form, it is evident from e data given before (p. 144), as also from Fig. 38, that the rtion of the solubility curve of the hexahydrate lying above is temperature represents *metastable* equilibria. The realiza-n of the metastable melting point of the hexahydrate is, erefore, due to suspended transformation. At the transition int, 29·8°, the solubility of the hexahydrate and α-tetrahy-ate is 100·6 parts of $CaCl_2$ in 100 parts of water.

The retroflex portion of the solubility curve of the hexa-drate extends to only 1° below the melting point of the drate. At 29·2° crystals of a new hydrate, β-tetrahydrate, parate out, and the solution, which now contains 112·8 parts $CaCl_2$ to 100 parts of water, is saturated with respect to the o hydrates. Throughout its whole extent the solubility curve DF of the β-tetrahydrate represents metastable equilibria. e upper limit of the solubility curve of β-tetrahydrate is ached at 38·4° (F), the point of intersection with the curve r the dihydrate.

Above 29·8° the stable hydrate is the α-tetrahydrate; and solubility curve extends to 45·3° (K), at which temperature cuts the solubility curve of the dihydrate. The curve of the tter hydrate extends to 175·5° (L), and is then succeeded by e curve for the monohydrate. The solubility curve of the hydrous salt does not begin until a temperature of about o°. The whole diagram, therefore, shows a succession of ble hydrates, a metastable hydrate, a metastable melting int and retroflex solubility curve.

Pressure-Temperature Diagram.—The complete study of e equilibria between the two components calcium chloride and water would require the discussion of the vapour pressure of the different systems, and its variation with the temperature. For our present purpose, however, such a discussion would not be of great value, and will therefore be omitted here; in general, the same relationships would be found as in the case of sodium sulphate (p. 136), except that the rounded portion of the solubility curve of the hexahydrate would be represented by a similar rounded portion in the pressure curve.[1] As in the case of sodium sulphate, the transition points of the different hydrates would be indicated by breaks in the curve of pressures. Finally, mention may again be made of the difference of the pressure of dissociation of the hexahydrate according as it becomes dehydrated to the α- or the β-tetrahydrate (p. 85).

The Indifferent Point.—We have already seen that at 30·2° calcium chloride hexahydrate melts completely in its water of crystallisation, and that, provided the pressure is maintained constant, addition or withdrawal of heat will cause the complete liquefaction or solidification, without the temperature of the system undergoing change. This behaviour, therefore, is similar to, but is not quite the same as the fusion of a simple substance such as ice; and the difference is due to the fact that in the case of the hexahydrate the emission of vapour by the liquid phase causes an alteration in the composition of the latter, owing to the non-volatility of the calcium chloride; whereas in the case of ice this is, of course, not so.

Consider, however, for the present that the vapour phase is absent, and that we are dealing with the two-phase system solid—solution. Then, since there are two components, the system is bivariant. For any given value of the pressure, therefore, we should expect that the system could exist a different temperatures; which, indeed, is the case. It has however, already been noted that when the composition of th liquid phase becomes the same as that of the solid, the syste then behaves as a *univariant* system; for, at a given pressur the system solid—solution can exist only at *one* temperatur change of temperature producing complete transformation one or other direction. *The variability of the system has therefore been diminished.*

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[1] See Roozeboom, *Zeitschr. physikal. Chem.*, 1889, 4. 31.

This behaviour will perhaps be more clearly understood when one reflects that since the composition of the two phases is the same, the system may be regarded as being formed of *one component*, just as the system $NH_4Cl \rightleftarrows NH_3 + HCl$ was regarded as being composed of one component when the vapour had the same total composition as the solid (p. 13). One component in two phases, however, constitutes a univariant system, and we can therefore see that calcium chloride hexahydrate in contact with solution of the same composition will constitute a univariant system. The temperature of equilibrium will, however, vary with the pressure;[1] if the latter is constant, the temperature will also be constant.

A point such as has just been referred to, which represents the special behaviour of a system of two (or more) components, in which the composition of two phases becomes identical, is known as an *indifferent point*,[2] and it has been shown[3] that at a given pressure the temperature in the indifferent point is the *maximum* or *minimum* temperature possible at the particular pressure[4] (cf. critical solution temperature). At such a point a system loses one degree of freedom, or behaves like a system of the next lower order.

The Hydrates of Ferric Chloride.—A better illustration of the formation of compounds possessing a definite melting point, and of the existence of retroflex solubility curves, is afforded by the hydrates of ferric chloride, which not only possess definite points of fusion, but these melting points are stable. A very brief description of the relations met with will suffice.[5]

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[1] Tammann, *Wied. Annalen*, 1899, **68**. 577.

[2] Duhem, *Journ. Physical Chem.*, 1898, **2**. 31.

[3] Gibbs, *Trans. Conn. Acad.*, **3**. 155; Saurel, *Journ. Phys. Chem.*, 1901, **5**. 35.

[4] In the case of the fusion of a compound of two components with formation of a liquid phase of the same composition, the temperature is a maximum; in the case of liquid mixtures of constant boiling-point, the temperature may be a minimum (p. 103).

[5] Roozeboom, *Zeitschr. physikal. Chem.*, 1892, **10**. 477. The formula of ferric chloride has been doubled, in order to avoid fractions in the expression of the water of crystallization.

Ferric chloride can form no less than four stable drates, viz. $Fe_2Cl_6,12H_2O$, $Fe_2Cl_6,7H_2O$, $Fe_2Cl_6,5H_2O$, $Fe_2Cl_6,4H_2O$, and each of these hydrates possesses a defi stable melting point. On analogy with the behaviour of cium chloride, therefore, we shall expect that the solubility cu of these different hydrates will exhibit a series of *tempera maxima;* the points of maximum temperature represen

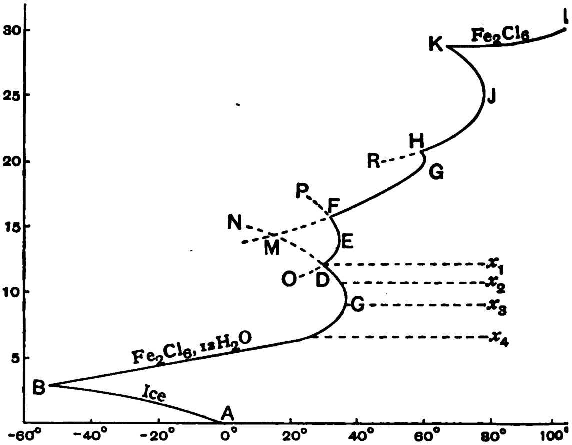

FIG. 39.

systems in which the composition of the solid and liquid p is the same. A graphical representation of the solu relations is given in Fig. 39, and the composition o different saturated solutions which can be formed is giv the following tables, the composition being expressed in cules of Fe_2Cl_6 to 100 molecules of water. The figures pr in thick type refer to transition and melting points.

COMPOSITION OF THE SATURATED SOLUTIONS OF FERRIC CHLORIDE AND ITS HYDRATES.

(*The name placed at the head of each table is the solid phase.*)

ICE.

Temperature.	Composition.
± −55°	± 2·75
−40°	2·37
−27·5°	1·90
−20·5°	1·64
−10°	1·00
0°	0

$Fe_2Cl_6,12H_2O$.

Temperature.	Composition.
−55°	± 2·75
−41°	2·81
−27°	2·98
0°	4·13
10°	4·54
20°	5·10
30°	5·93
35°	6·78
36·5°	7·93
37°	8·33
36°	9·29
33°	10·45
30°	11·20
27·4°	12·15
20°	12·83
10°	13·20
8°	13·70

$Fe_2Cl_6,7H_2O$.

Temperature.	Composition.
20°	11·35
27·4°	12·15
32°	13·55
32·5°	14·29
30°	15·12
25°	15·54

$Fe_2Cl_6,5H_2O$.

Temperature.	Composition.
12°	12·87
20°	13·95
27°	14·85
30°	15·12
35°	15·64
50°	17·50
55°	19·15
56°	20·00
55°	20·32

Fe_2Cl_6 (ANHYDROUS).

Temperature.	Composition.
66°	29·20
70°	29·42
75°	28·92
80°	29·20
100°	29·75

$Fe_2Cl_6,4H_2O$.

Temperature.	Composition.
50°	19·96
55°	20·32
60°	20·70
69°	21·53
72·5°	23·35
73·5°	25·00
72·5°	26·15
70°	27·90
66°	29·20

The lowest portion of the curve, AB, represents the equilibria between ice and solutions containing ferric chloride. It represents, in other words, the lowering of the fusion point of ice by addition of ferric chloride. At the point B (−55°), the cryohydric point (p. 115) is reached, at which the solution is in equilibrium with ice and ferric chloride dodecahydrate. As has already been shown, such a point represents an invariant system; and the liquid phase will, therefore, solidify to a mixture of ice and hydrate without change of temperature. If heat is added, ice will melt and the system will pass to the curve BCDN, which is the solubility curve of the dodecahydrate. At C (37°), the point of maximum temperature, the hydrate melts completely. The retroflex portion of this curve can be followed backwards to a temperature of 8°, but below 27·4° (D), the solutions are supersaturated with respect to the heptahydrate; point D is the eutectic point for dodecahydrate and heptahydrate. The curve DEF is the solubility curve of the heptahydrate, E being the melting point, 32·5°. On further increasing the quantity of ferric chloride, the temperature of equilibrium is lowered until at F (30°) another eutectic point is reached, at which the heptahydrate and pentahydrate can co-exist with solution. Then follow the solubility curves for the pentahydrate, the tetrahydrate, and the anhydrous salt; G (56°) is the melting point of the former hydrate, J (73·5°) the melting point of the latter. H and K, the points at which the curves intersect, represent eutectic points; the temperature of the former is 55°, that of the latter 66°. The dotted portions of the curves represent metastable equilibria.

As is seen from the diagram, a remarkable series of solubility curves is obtained, each passing through a point of maximum temperature, the whole series of curves forming an undulating "festoon." To the right of the series of curves the diagram represents unsaturated solutions; to the left, supersaturated.

If an unsaturated solution, the composition of which is represented by a point in the field to the right of the solubility curves, is cooled down, the result obtained will differ according as the composition of the solution is the same as that of a cryohydric point, or of a melting point, or has an intermediate value. Thus, if a solution represented by x_1 is cooled down, the composition will remain unchanged as indicated by the horizontal dotted line, until the point D is reached. At this point, dodecahydrate and heptahydrate will separate out, and the liquid will ultimately solidify completely to a mixture or "conglomerate" of these two hydrates; the temperature of he system remaining constant until complete solidification has iken place. If, on the other hand, a solution of the composiion x_3 is cooled down, ferric chloride dodecahydrate will be ormed when the temperature has fallen to that represented by C, and the solution will completely solidify, without alteraion of temperature, with formation of this hydrate. In both hese cases, therefore, a point is reached at which complete solidification occurs without change of temperature.

Somewhat different, however, is the result when the solution has an intermediate composition, as represented by x_2 or x_4. In the former case the dodecahydrate will first of all separate out, but on further withdrawal of heat the temperature will fall, the solution will become relatively richer in ferric chloride, owing to separation of the hydrate, and ultimately the eutectic point D will be reached, at which complete solidification will occur. Similarly with the second solution. Ferric chloride dodecahydrate will first be formed, and the temperature will gradually fall, the composition of the solution following the curve CB until the cryohydric point B is reached, when the whole will solidify to a conglomerate of ice and dodecahydrate.

Suspended Transformation.—Not only can the upper branch of the solubility curve of the dodecahydrate be followed backwards to a temperature of 8°, or about 19° below the temperature of transition to the heptahydrate; but suspended transformation has also been observed in the case of the heptahydrate and the pentahydrate. To such an extent is this the case that the solubility curve of the latter hydrate has been followed downwards to its point of intersection with the curve for the dodecahydrate. This point of intersection, represented in Fig. 39 by M, lies at a temperature of about 15°; and at this temperature, therefore, it is possible for the two solid phases dodecahydrate and pentahydrate to coexist, so that M is a eutectic point for the dodecahydrate and the pentahydrate. It is, however, a metastable eutectic point, for it lies in the region of supersaturation with respect to the heptahydrate; and it can be realized only because of the fact that the latter hydrate is not readily formed.

Evaporation of Solutions at Constant Temperature.—On of water; those under the heading "composition," the num of gram-molecules of water in the solution to one gr molecule of $CaCl_2$.

SOLUBILITY OF CALCIUM CHLORIDE HEXAHYDRATE.

Temperature.	Solubility.	Composition.
−55°	42·5	14·5
−25°	50·0	12·3
−10°	55·0	11·2
0°	59·5	10·37
10°	65·0	9·49
20°	74·5	8·28
25°	82·0	7·52
28·5°	90·5	6·81
29·5°	95·5	6·46
30·2°	102·7	6·00
29·6°	109·0	5·70
29·2°	112·8	5·41

So far as the first portion of the curve is concerne resembles the most general type of solubility curve. In present case the solubility is so great and increases so ra with rise of temperature, that a point is reached at whic water of crystallization of the salt is sufficient for its com solution. This temperature is 30·2°; and since the compos of the solution is the same as that of the solid salt, viz. 1 of $CaCl_2$ to 6 mols. of water, this temperature must b melting point of the hexahydrate. At this point the hy will fuse or the solution will solidify without change of tem ture and without change of composition.

But the solubility curve of calcium chloride hexahy differs markedly from the other solubility curves hitherto sidered in that it possesses a *retroflex portion*, represent the figure by BC. As is evident from the figure, there calcium chloride hexahydrate exhibits the peculiar and, was at first thought, impossible behaviour that it can equilibrium at one and the same temperature with two diff solutions, one of which contains more, the other less, than the solid hydrate; for it must be remembered would be still more bewildering. The composition of the different solutions formed will be represented by the perpendicular line $x_2 12345$. Evaporation will first cause the separation of the dodecahydrate, and then total disappearance of the liquid phase. Then liquefaction will occur, and the system will now be represented by the point 2, in which condition it will remain until the solid hydrate has disappeared. Following this there will be deposition of the heptahydrate (point 3), with subsequent disappearance of the liquid phase. Further dehydration will again cause liquefaction, when the concentration of the solution will be represented by the point 4; the heptahydrate will ultimately disappear, and then will ensue the deposition of the pentahydrate, and complete solidification will result. On evaporating a solution, therefore, of the composition x_2, the following series of phenomena will be observed: solidification to dodecahydrate; liquefaction; solidification to heptahydrate; liquefaction; solidification to pentahydrate.[1]

Although ferric chloride and water form the largest and best-studied series of hydrates possessing definite melting points, examples of similar hydrates are not few in number; and more careful investigation is constantly adding to the list. In all these cases the solubility curve will show a point of maximum temperature, at which the hydrate melts, and will end, above and below, in a cryohydric point. Conversely, if such a curve is found in a system of two components, we can argue that a definite compound of the components possessing a definite melting point is formed.

Inevaporable Solutions.—If a saturated solution in contact with two hydrates, or with a hydrate and anhydrous salt is heated, the temperature and composition of the solution will, of course, remain unchanged so long as the two solid phases are present, for such a system is invariant. In addition to this, however, the *quantity* of the solution will also remain unchanged, the water which evaporates being supplied by the higher hydrate. The same phenomenon is also observed in the case of cryohydric points when ice is a solid phase; so long as the latter is present, evaporation will be accompanied by fusion of the ice, and the quantity of solution will remain constant. Such solutions are called *inevaporable*.[1]

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1892, **10**. 477.

Illustration.—In order to illustrate the application of the principles of the Phase Rule to the study of systems formed by a volatile and a non-volatile component, a brief description may be given of the behaviour of sulphur dioxide and potassium iodide, which has formed the subject of a recent investigation. After it had been found[2] that liquid sulphur dioxide has the property of dissolving potassium iodide, and that the solutions thus obtained present certain peculiarities of behaviour, the question arose as to whether or not compounds are formed between the sulphur dioxide and the potassium iodide, and if so, what these compounds are. To find an answer to this question, Walden and Centnerszwer[3] made a complete investigation of the solubility curves (equilibrium curves) of these two components, the investigation extending from the freezing point to the critical point of sulphur dioxide. For convenience of reference, the results which they obtained are represented diagrammatically in Fig. 41. The freezing point (A) of pure sulphur dioxide was found to be −72·7°. Addition of potassium iodide lowered the freezing point, but the maximum depression obtained was very small, and was reached when the concentration of the potassium iodide in the solution was only 0.336 mols. per cent. Beyond this point, an increase in the concentration of the iodide was accompanied by an elevation of the freezing point, the change of the freezing point with the concentration being represented by the curve BC. The solid

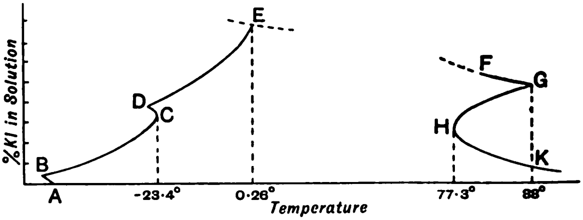

FIG. 41.

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[1] Meyerhoffer, *Ber.*, 1897, 30. 1810.
[2] Walden, *Ber.*, 1899, 32. 2863.
[3] *Zeitschr. physikal. Chem.*, 1903, 42. 432.

hich separated from the solutions represented by BC was a right *yellow* crystalline substance. At the point C ($-23\cdot4^\circ$) temperature-maximum was reached; and as the concentration of the potassium iodide was continuously increased, the emperature of equilibrium first fell and then slowly rose, until t $+0\cdot26^\circ$ (E) a second temperature-maximum was registered. On passing the point D, the solid which was deposited from the solution was a *red* crystalline substance. On withdrawing sulphur dioxide from the system, the solution became turbid, and the temperature remained constant. The investigation was not pursued farther at this point, the attention being then directed to the equilibria at higher temperatures.

When a solution of potassium iodide in liquid sulphur dioxide containing 1·49 per cent. of potassium iodide was heated, solid (potassium iodide) was deposited at a temperature of 96·4°. Solutions containing more than about 3 per cent. of the iodide separated, on being heated, into two layers, and the temperature at which the liquid became heterogeneous fell as the concentration was increased; a temperature-minimum being obtained with solutions containing 12 per cent. of potassium iodide. On the other hand, solutions containing 30·9 per cent. of the iodide, on being heated, deposited potassium iodide; while a solution containing 24·5 per cent. of the salt first separated into two layers at 89·3°, and then, on cooling, solid was deposited and one of the liquid layers disappeared.

Such are, in brief, the results of experiment; their interpretation in the light of the Phase Rule is the following:—

The curve AB is the freezing-point curve of solid sulphur dioxide in contact with solutions of potassium iodide. BCD is the solubility curve of the *yellow* crystalline solid which is deposited from the solutions. C, the temperature-maximum, is the melting point of this yellow solid, and the composition of the latter must be the same as that of the solution at this point (p. 143), which was found to be that represented by the ormula $KI,14SO_2$. B is therefore the eutectic point, at which olid sulphur dioxide and the compound $KI,14SO_2$ can exist ogether in equilibrium with solution and vapour. The curve E is the solubility curve of the *red* crystalline solid, and the and water would require the discussion of the vapour press of the different systems, and its variation with the temperatu For our present purpose, however, such a discussion wo not be of great value, and will therefore be omitted here; general, the same relationships would be found as in the c of sodium sulphate (p. 136), except that the rounded portio the solubility curve of the hexahydrate would be represen by a similar rounded portion in the pressure curve.[1] As the case of sodium sulphate, the transition points of different hydrates would be indicated by breaks in the cu of pressures. Finally, mention may again be made of difference of the pressure of dissociation of the hexahyd according as it becomes dehydrated to the α- or the β-te hydrate (p. 85).

The Indifferent Point.—We have already seen that at 3 calcium chloride hexahydrate melts completely in its wate crystallisation, and that, provided the pressure is maintai constant, addition or withdrawal of heat will cause the comp liquefaction or solidification, without the temperature of system undergoing change. This behaviour, therefore similar to, but is not quite the same as the fusion of a sin substance such as ice; and the difference is due to the that in the case of the hexahydrate the emission of vapou the liquid phase causes an alteration in the composition of latter, owing to the non-volatility of the calcium chlor whereas in the case of ice this is, of course, not so.

Consider, however, for the present that the vapour p is absent, and that we are dealing with the two-phase sys solid—solution. Then, since there are two components, system is bivariant. For any given value of the press therefore, we should expect that the system could exis different temperatures; which, indeed, is the case. It however, already been noted that when the composition of liquid phase becomes the same as that of the solid, the sys then behaves as a *univariant* system; for, at a given press the system solid—solution can exist only at *one* temperat change of temperature producing complete transformatio ie or other direction. *The variability of the system has erefore been diminished.*

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[1] See Roozeboom, *Zeitschr. physikal. Chem.*, 1889, **4**. 31.

This behaviour will perhaps be more clearly understood hen one reflects that since the composition of the two phases the same, the system may be regarded as being formed of *e component*, just as the system $NH_4Cl \rightleftarrows NH_3 + HCl$ was garded as being composed of one component when the ipour had the same total composition as the solid (p. 13). ne component in two phases, however, constitutes a uniriant system, and we can therefore see that calcium chloride xahydrate in contact with solution of the same composition ill constitute a univariant system. The temperature of uilibrium will, however, vary with the pressure;[1] if the tter is constant, the temperature will also be constant.

A point such as has just been referred to, which represents e special behaviour of a system of two (or more) components, which the composition of two phases becomes identical, is iown as an *indifferent point*,[2] and it has been shown[3] that at given pressure the temperature in the indifferent point is the *aximum* or *minimum* temperature possible at the particular essure[4] (cf. critical solution temperature). At such a point system loses one degree of freedom, or behaves like a system the next lower order.

The Hydrates of Ferric Chloride.—A better illustration of e formation of compounds possessing a definite melting point, d of the existence of retroflex solubility curves, is afforded the hydrates of ferric chloride, which not only possess efinite points of fusion, but these melting points are stable. very brief description of the relations met with will suffice.[5]

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[1] Tammann, *Wied. Annalen*, 1899, **68**. 577.

[2] Duhem, *Journ. Physical Chem.*, 1898, **2**. 31.

[3] Gibbs, *Trans. Conn. Acad.*, **3**. 155; Saurel, *Journ. Phys. Chem.*, 01, **5**. 35.

[4] In the case of the fusion of a compound of two components with rmation of a liquid phase of the same composition, the temperature is a aximum; in the case of liquid mixtures of constant boiling-point, the mperature may be a minimum (p. 103).

[5] Roozeboom, *Zeitschr. physikal. Chem.*, 1892, **10**. 477. The formula ferric chloride has been doubled, in order to avoid fractions in the pression of the water of crystallization.

relations between concentration and temperature, with the hel of the accompanying diagram, Fig. 42.

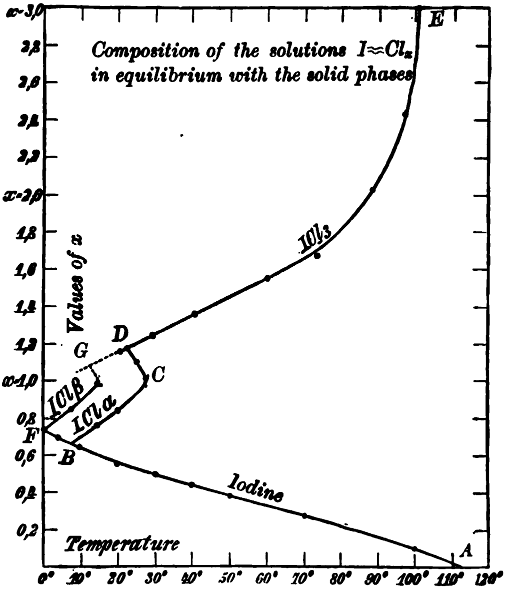

FIG. 42.

Concentration-Temperature Diagram.—In this diagram temperatures are taken as the abscissæ, and the composition the solution, expressed in atoms of chlorine to one atom iodine,[1] is represented by the ordinates. In the diagram, represents the melting point of pure iodine, 114°. If chlor is added to the system, a solution of chlorine in liquid iod is obtained, and the temperature at which solid iodine is equilibrium with the liquid solution will be all the lower greater the concentration of the chlorine. We therefore obt the curve ABF, which represents the composition of the soluti which solid iodine is in equilibrium at different tempera- s. This curve can be followed down to 0°, but at tempera- s below 7·9° (B) it represents metastable equilibria. At B ne monochloride can be formed, and if present the system omes invariant; B is therefore a quadruple point at which four phases, iodine, iodine monochloride, solution, and our, can coexist. Continued withdrawal of heat at this it will therefore lead to the complete solidification of the tion to a mixture or conglomerate of iodine and iodine ochloride, while the temperature remains constant during process. B is the eutectic point for iodine and iodine ochloride.

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[1] The composition of a solution is represented symbolically by plac a double wavy line between the symbols of the components, and in cating the number of atoms present in the ordinary manner: th I ≈ Cl$_x$ represents a solution containing x atoms of chlorine to atom of iodine (Roozeboom, *Zeitschr. physikal. Chem.*, 1888, **2**. 450).

Just as we found in the case of aqueous salt solutions that emperatures above the cryohydric or eutectic point, two rent solutions could exist, one in equilibrium with ice, the r in equilibrium with the salt (or salt hydrate), so in the of iodine and chlorine there can be two solutions above eutectic point B, one containing a lower proportion of rine in equilibrium with iodine, the other containing a er proportion of chlorine in equilibrium with iodine mono- ride. The composition of the latter solution is represented the curve BCD. As the concentration of chlorine is eased, the temperature at which there is equilibrium between ne monochloride and solution rises until a point is reached hich the composition of the solution is the same as that of solid. At this point (C), iodine monochloride melts. lition of one of the components will lower the temperature fusion, and a continuous curve,[1] exhibiting a retroflex tion as in the case of $CaCl_2,6H_2O$, will be obtained. At peratures below its melting point, therefore, iodine mono- oride can be in equilibrium with two different solutions.

The upper portion of this curve, CD, can be followed mwards to a temperature of 22·7°. At this temperature ine trichloride can separate out, and a second quadruple nt (D) is obtained. This is the eutectic point for iodine nochloride and iodine trichloride.

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[1] Since iodine monochloride in the liquid state is only very slightly ociated, the bend at C is very sharp (see p. 145, footnote).

By addition of heat and increase in the amount of chlorine the iodine monochloride disappears, and the system passes along the curve DE, which represents the composition of the solutions in equilibrium with solid iodine trichloride. The concentration of chlorine in the solution increases as the temperature is raised, until at the point E, where the solution has the same composition as the solid, the maximum temperature is reached; the iodine trichloride melts. On increasing still further the concentration of chlorine in the solution, the temperature of equilibrium falls, and a continuous curve, similar to that for the monochloride, is obtained. The upper branch of this curve has been followed down to a temperature of 30°, the solution at this point containing 99·6 per cent. of chlorine.[1] The very rounded form of the curve is due to the trichloride being largely dissociated in the liquid state.

One curve still remains to be considered. As has already been mentioned, iodine monochloride can exist in two crystalline forms, only one of which, however, is stable at temperatures below the melting point; the two forms are *monotropic* (p. 42). The stable form which melts at 27·2°, is called the α-form, while the less stable variety, melting at 13·9°, is known as the β-form. If, now, the presence of α-ICl is excluded, it is possible to obtain the β-form, and to study the conditions of equilibrium between it and solutions of iodine and chlorine, from the eutectic point F to the melting point G. As the β-ICl becomes less stable in presence of excess of chlorine, it has not been possible to study the retroflex portion of the curve represented by the dotted continuation of FG.

The following table gives some of the numerical data from which Fig. 42 was constructed.[2]

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[1] This upper branch of the curve is not shown in the figure, as the ordinate corresponding to 30° would be very great.

[2] Stortenbeker, *Zeitschr. physikal. Chem.*, 1889, 3. 22.

he system remaining constant until complete solidification has aken place. If, on the other hand, a solution of the composiion x_3 is cooled down, ferric chloride dodecahydrate will be ormed when the temperature has fallen to that represented by C, and the solution will completely solidify, without alteraion of temperature, with formation of this hydrate. In both hese cases, therefore, a point is reached at which complete olidification occurs without change of temperature.

Somewhat different, however, is the result when the solution as an intermediate composition, as represented by x_2 or x_4. n the former case the dodecahydrate will first of all separate ut, but on further withdrawal of heat the temperature will all, the solution will become relatively richer in ferric chloride, wing to separation of the hydrate, and ultimately the eutectic oint D will be reached, at which complete solidification will ccur. Similarly with the second solution. Ferric chloride odecahydrate will first be formed, and the temperature will radually fall, the composition of the solution following the urve CB until the cryohydric point B is reached, when the hole will solidify to a conglomerate of ice and dodecahydrate.

Suspended Transformation.—Not only can the upper branch f the solubility curve of the dodecahydrate be followed backards to a temperature of 8°, or about 19° below the temperature of transition to the heptahydrate; but suspended ansformation has also been observed in the case of the eptahydrate and the pentahydrate. To such an extent is this e case that the solubility curve of the latter hydrate has been llowed downwards to its point of intersection with the curve r the dodecahydrate. This point of intersection, represented Fig. 39 by M, lies at a temperature of about 15°; and at this mperature, therefore, it is possible for the two solid phases odecahydrate and pentahydrate to coexist, so that M is a tectic point for the dodecahydrate and the pentahydrate. It , however, a metastable eutectic point, for it lies in the region upersaturation with respect to the heptahydrate; and it can realized only because of the fact that the latter hydrate is t readily formed.

vaporation of Solutions at Constant Temperature.—On

evaporating dilute solutions of ferric chloride at consta
perature, a remarkable series of changes is observed,
however, will be und
with the help of
Suppose an unsatur
lution, the composi
which is represented
point x_1, is evaporat
temperature of ab
− 18°. As water
off, the composition
solution will foll
dotted line of const
perature, until at th
where it cuts the curve BC the solid hydrate Fe_2Cl_6
separates out. As water continues to be removed, the
must be deposited (in order that the solution shall
saturated), until finally the solution dries up to the
As dehydration proceeds, the heptahydrate can be form
the dodecahydrate will finally pass into the heptahydrat
this, in turn, into the pentahydrate.

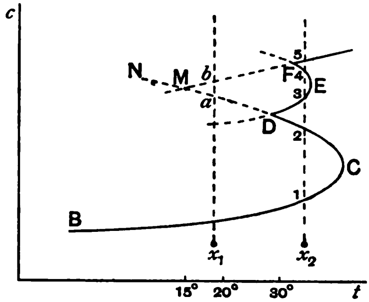

Fig. 40.

But the heptahydrate is not always formed by the d
tion of the dodecahydrate, and the behaviour on evapo
therefore somewhat perplexing at first sight. After the
has dried to the dodecahydrate, as explained above,
removal of water causes liquefaction, and the system
represented by the point of intersection at *a*; at this p
solid hydrate is in equilibrium with a solution contain
tively more ferric chloride. If, therefore, evaporation
tinued, the solid hydrate must *pass into solution* in or
the composition of the latter may remain unchanged,
ultimately a liquid will again be obtained. A ver
further dehydration will bring the solution into the stat
sented by *b*, at which the pentahydrate is formed, a
solution will at last disappear and leave this hydrate alo

Without the information to be obtained from the cu
Figs. 39 and 40, the phenomena which would be obser
carrying out the evaporation at a temperature of about

would be still more bewildering. The composition of the different solutions formed will be represented by the perpendicular line $x_2 12345$. Evaporation will first cause the separation of the dodecahydrate, and then total disappearance of the liquid phase. Then liquefaction will occur, and the system will now be represented by the point 2, in which condition it will remain until the solid hydrate has disappeared. Following this there will be deposition of the heptahydrate (point 3), with subsequent disappearance of the liquid phase. Further dehydration will again cause liquefaction, when the concentration of the solution will be represented by the point 4; the heptahydrate will ultimately disappear, and then will ensue the deposition of the pentahydrate, and complete solidification will result. On evaporating a solution, therefore, of the composition x_2, the following series of phenomena will be observed: solidification to dodecahydrate; liquefaction; solidification to heptahydrate; liquefaction; solidification to pentahydrate.[1]

Although ferric chloride and water form the largest and best-studied series of hydrates possessing definite melting points, examples of similar hydrates are not few in number; and more careful investigation is constantly adding to the list. In all these cases the solubility curve will show a point of maximum temperature, at which the hydrate melts, and will end, above and below, in a cryohydric point. Conversely, if such a curve is found in a system of two components, we can argue that a definite compound of the components possessing a definite melting point is formed.

Inevaporable Solutions.—If a saturated solution in contact with two hydrates, or with a hydrate and anhydrous salt is heated, the temperature and composition of the solution will, of course, remain unchanged so long as the two solid phases are present, for such a system is invariant. In addition to this, however, the *quantity* of the solution will also remain unchanged, the water which evaporates being supplied by the higher hydrate. The same phenomenon is also observed in the case of cryohydric points when ice is a solid phase; so long as the latter is present, evaporation will be accompanied by fusion of the ice, and the quantity of solution will remain constant. Such solutions are called *inevaporable*.[1]

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1892, **10**. 477.

Illustration.—In order to illustrate the application of the principles of the Phase Rule to the study of systems formed by a volatile and a non-volatile component, a brief description may be given of the behaviour of sulphur dioxide and potassium iodide, which has formed the subject of a recent investigation. After it had been found[2] that liquid sulphur dioxide has the property of dissolving potassium iodide, and that the solutions thus obtained present certain peculiarities of behaviour, the question arose as to whether or not compounds are formed between the sulphur dioxide and the potassium iodide, and if so, what these compounds are. To find an answer to this question, Walden and Centnerszwer[3] made a complete investigation of the solubility curves (equilibrium curves) of these two components, the investigation extending from the freezing point to the critical point of sulphur dioxide. For convenience of reference, the results which they obtained are represented diagrammatically in Fig. 41. The freezing point (A) of pure sulphur dioxide was found to be −72·7°. Addition of potassium iodide lowered the freezing point, but the maximum depression obtained was very small, and was reached when the concentration of the potassium iodide in the solution was only 0.336 mols. per cent. Beyond this point, an increase in the concentration of the iodide was accompanied by an elevation of the freezing point, the change of the freezing point with the concentration being represented by the curve BC. The solid

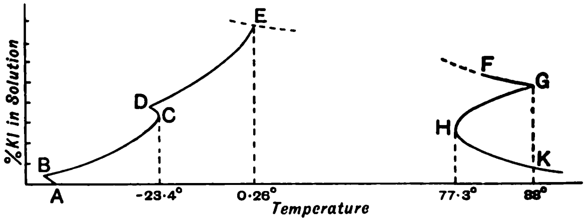

FIG. 41.

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[1] Meyerhoffer, *Ber.*, 1897, **30**. 1810.

[2] Walden, *Ber.*, 1899, **32**. 2863.

[3] *Zeitschr. physikal. Chem.*, 1903, **42**. 432.

solution, solid iodine monochloride must separate out in order that the concentration of the solution remain unchanged.[1] As the result, therefore, we obtain the bivariant system iodine monochloride—vapour.

A detailed discussion of the effect of a continued increase of pressure will not be necessary. From what has already been said and with the help of Fig. 44, it will readily be understood that this will lead successively to the univariant system (*c*), iodine monochloride—solution—vapour; the bivariant system solution—vapour (field II.); the univariant system (*d*), iodine trichloride—solution—vapour; and the bivariant system x', iodine trichloride—vapour. If the temperature of the experiment is above the melting point of the monochloride, then the systems in which this compound occurs will not be formed.

Sulphur Dioxide and Water.—In the case just studied we have seen that the components can combine to form definite compounds possessing stable melting points. The curves of equilibrium, therefore, resemble in their general aspect those of calcium chloride and water, or of ferric chloride and water. In the case of sulphur dioxide and water, however, the melting point of the compound formed cannot be realized, because transition to another system occurs; retroflex concentration-temperature curves are therefore not found here, but the curves exhibit breaks or sudden changes in direction at the transition points, as in the case of the systems formed by sodium sulphate and water. The case of sulphur dioxide and water is also of interest from the fact that two liquid phases can be formed.

The phases which occur are—Solid: ice, sulphur dioxide hydrate, $SO_2,7H_2O$. Liquid: two solutions, the one containing excess of sulphur dioxide, the other excess of water, and represented by the symbols $SO_2 \leftrightharpoons xH_2O$ (solution I.), and $H_2O \leftrightharpoons ySO_2$ (solution II.). Vapour: a mixture of sulphur dioxide and water vapour in varying proportions. Since there are two components, sulphur dioxide and water, the number of possible systems is considerable. Only the following, however, have been studied :—

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[1] At point *b* the ratio of chlorine to iodine in the solution is less than in the monochloride, so that by the separation of this the excess of chlorine yielded by the *condensation of* the vapour is removed.

I. *Invariant Systems : Four co-existing phases.*
  (*a*) Ice, hydrate, solution, vapour.
  (*b*) Hydrate, solution I., solution II., vapour.

II. *Univariant Systems : Three co-existing phases.*
  (*a*) Hydrate, solution I., vapour.
  (*b*) Hydrate, solution II., vapour.
  (*c*) Solution I., solution II., vapour.
  (*d*) Hydrate, solution I., solution II.
  (*e*) Hydrate, ice, vapour.
  (*f*) Ice, solution II., vapour.
  (*g*) Ice, hydrate, solution II.

III. *Bivariant Systems : Two co-existing phases.*
  (*a*) Hydrate, solution I.
  (*b*) Hydrate, solution II.
  (*c*) Hydrate, vapour.
  (*d*) Hydrate, ice.
  (*e*) Solution I., solution II.
  (*f*) Solution I., vapour.
  (*g*) Solution I., ice.
  (*h*) Solution II., vapour.
  (*i*) Solution II., ice.
  (*j*) Ice, vapour.

Pressure-Temperature Diagram.[1]—If sulphur dioxide is passed into water at 0°, a solution will be formed and the temperature at which ice can exist in equilibrium with this solution will fall more and more as the concentration of the sulphur dioxide increases. At $-2{\cdot}6°$, however, a cryohydric point is reached at which solid hydrate separates out, and the system becomes invariant. The curve AB (Fig. 45) therefore represents the pressure of the system ice—solution II.—vapour, and B represents the temperature and pressure at which the invariant system ice—hydrate—solution II.—vapour can exist. At this point the temperature is $-2{\cdot}6°$, and the pressure 21·1 cm. If heat is withdrawn from this system, the solution will ultimately lify to a mixture of ice and hydrate, and there will be ined the univariant system ice—hydrate—vapour. The our pressure of this system has been determined down to a perature of $-9{\cdot}5°$, at which temperature the pressure unts to 15 cm. The pressures for this system are repre- ed by the curve BC. If at the point B the volume is inished, the pressure must remain constant, but the relative unts of the different phases will undergo change. If suit- quantities of these are present, diminution of volume will ately lead to the total condensation of the vapour phase,

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[1] Roozeboom, *Rec. trav. chim. Pays-Bas*, 1884, **3**. 29 ; 1885, **4**. 65 ; *Zeitschr. physikal. Chem.*, 1888, **2**, 450.

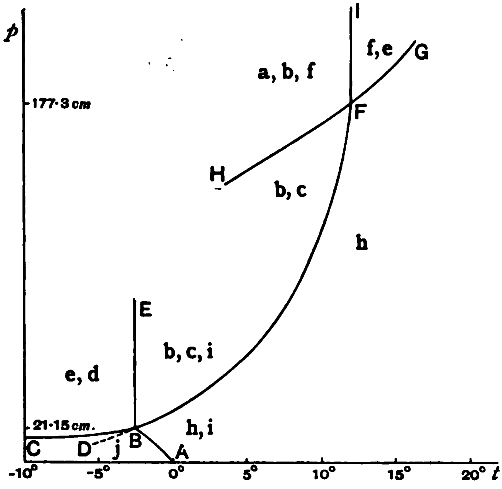

FIG. 45.

there will remain the univariant system ice—hydrate—solu- . The temperature of equilibrium of this system will alter the pressure, but, as in the case of the melting point of a ple substance, great differences of pressure will cause only parativelysmall changes in the temperature of equilibrium. change of the cryohydric point with the pressure is resented by the line BE; the actual values have not been ermined, but the curve must slope towards the pressure axis ause fusion is accompanied by diminution of volume, as in case of pure ice.

A fourth univariant system can be formed at B. This is the system hydrate—solution II.—vapour. The conditions for the existence of this system are represented by the curve BF, which may therefore be regarded as the vapour-pressure curve of the saturated solution of sulphur dioxide heptahydrate in water. Unlike the curve for iodine trichloride—solution—vapour, this curve cannot be followed to the melting point of the hydrate. Before this point is reached, a second liquid phase appears, and an invariant system consisting of hydrate—solution I.—solution II.—vapour is formed. We have here, therefore, the phenomenon of melting under the solution as in the case of succinic nitrile and water (p. 120). This point is represented in the diagram by F; the temperature at this point is 12·1°, and the pressure 177·3 cm. The range of stable existence of the hydrate is therefore from −2·6° to 12·1°; nevertheless, the curve FB has been followed down to a temperature of −6°, at which point ice formed spontaneously.

So long as the four phases hydrate, two liquid phases, and vapour are present, the condition of the system is perfectly defined. By altering the conditions, however, one of the phases can be made to disappear, and a univariant system will then be obtained. Thus, if the vapour phase is made to disappear, the univariant system solution I.—solution II.—hydrate, will be left, and the temperature at which this system is in equilibrium will vary with the pressure. This is represented by the curve FI; under a pressure of 225 atm. the temperature of equilibrium is 17·1°. Increase of pressure, therefore, raises the temperature at which the three phases can coexist.

Again, addition of heat to the invariant system at F will cause the disappearance of the solid phase, and there will be formed the univariant system solution I.—solution II.—vapour. In the case of this system the vapour pressure increases as the temperature rises, as represented by the curve FG. Such a system is analogous to the case of ether and water, or other two partially miscible liquids (p. 101). As the temperature changes, the composition of the two liquid phases will undergo change; but this system has not been studied fully.

The fourth curve, which ends at the quadruple point F, is that representing the vapour pressure of the system hydrate—solution I.—vapour (FH). This curve has been followed to a temperature of 0°, the pressure at this point being 113 cm. The metastable prolongation of GF has also been determined. Although, theoretically, this curve must lie below FH, it was found that the difference in the pressure for the two curves was within the error of experiment.

Bivariant Systems.—The different bivariant systems, consisting of two phases, which can exist within the range of temperature and pressure included in Fig. 45, were given on p. 168. The conditions under which these systems can exist are represented by the areas in the diagram, and the fields of the different bivariant systems are indicated by letters, corresponding to the letters on p. 168. Just as in the case of one-component systems (p. 27), we found that the field lying between any two curves gave the conditions of existence of that phase which was common to the two curves, so also in the case of two-component systems, a bivariant two-phase system occurs in the field enclosed[1] by the two curves to which the two phases are common. As can be seen, the same bivariant system can occur in more than one field.

As is evident from Fig. 45, three different bivariant systems are capable of existing in the area HFI; which of these will be obtained will depend on the relative masses of the different phases in the univariant or invariant system. Thus, starting with a system represented by a point on the curve HF, diminution of volume at constant temperature will cause the condensation of a portion of the vapour, which is rich in sulphur dioxide; since this would increase the concentration of sulphur dioxide in the solution, it must be counteracted by the passage of a portion of the hydrate (which is relatively poor in sulphur dioxide) into the solution. If, therefore, the amount of hydrate present is relatively very small, the final result of the compression will be the production of the system *f*, solution I.—vapour. On the other hand, if the vapour is present in relatively small amount, it will be the first phase to disappear, and the bivariant system *a*, hydrate—solution I., will be obtained. Finally, if we start with the invariant system at F, compression will cause the condensation of vapour, while the composition of the two solutions will remain unchanged. When all the vapour has disappeared, the univariant system hydrate—solution I.—solution II. will be left. If, now, the pressure is still further increased, while the temperature is kept below 12°, more and more hydrate must be formed at the expense of the two liquid phases (because 12° is the lower limit for the coexistence of the two liquid phases), and if the amount of the solution I. (containing excess of sulphur dioxide) is relatively small, it will disappear before solution II., and there will be obtained the bivariant system hydrate—solution II. (bivariant system *b*).

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[1] Two curves "enclose" a field when they form with one another an angle less than two right angles.

In a similar manner, account can be taken of the formation of the other bivariant systems.

A behaviour similar to that of sulphur dioxide and water is shown by chlorine and water and by bromine and water, although these have not been so fully studied.[1] In the case of hydrogen bromide and water, and of hydrogen chloride and water, a hydrate, viz. $HBr,2H_2O$ and $HCl,2H_2O$, is formed which possesses a definite melting point, as in the case of iodine trichloride. In these cases, therefore, a retroflex curve is obtained. Further, just as in the case of the chlorides of iodine the upper branch of the retroflex curve ended in a eutectic point, so also in the case of the hydrate $HBr,2H_2O$ the upper branch of the curve ends in a eutectic point at which the system dihydrate—monohydrate—solution—vapour can exist. Before the melting point of the monohydrate is reached, two liquid phases are formed, as in the case of sulphur dioxide and water.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, *loc. cit.*

CHAPTER X

SOLID SOLUTIONS. MIXED CRYSTALS

General.—With the conception of gaseous and liquid solutions, every one is familiar. Gases can mix in all proportions to form homogeneous solutions. Gases can dissolve in or be "absorbed" by liquids; and solids, also, when brought in contact with liquids, "pass into solution" and yield a homogeneous liquid phase. On the other hand, the conception of a *solid solution* is one which in many cases is found more difficult to appreciate; and the existence and behaviour of solid solutions, in spite of their not uncommon occurrence and importance, are in general comparatively little known.

The reason of this is to be found, to some extent, no doubt, in the fact that the term "solid solution" was introduced at a comparatively recent date,[1] but it is probably also due in some measure to a somewhat hazy comprehension of the definition of the term "solution" itself. As has already been said (p. 90), a solution is a homogeneous phase, the composition of which can vary continuously within certain limits; the definition involves, therefore, no condition as to the physical state of the substances. Accordingly, solid solutions are homogeneous solid phases, the composition of which can undergo continuous variation within certain limits. Just as we saw that the range of variation of composition is more limited in the case of liquids than in the case of gases, so also we find that the limits of miscibility are in general still more restricted in the case of solids. Examples of complete miscibility are, however, not unknown even in the case of solid substances.

Solid solutions have long been known, although, of course, they were not defined as such. Thus, the phenomena of "occlusion" of gases by metals and other substances (occlusion of hydrogen by palladium; occlusion of hydrogen by iron) are due to the formation of solid solutions. The same is probably also true of the phenomena of "adsorption," as in the removal of organic colouring matter by charcoal, although, in this case, surface tension no doubt plays a considerable part.[1]

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[1] Van't Hoff, *Zeitschr. physikal. Chem.*, 1890, **5**. 323.

As examples of the solution of gases in solids there may be cited (in addition to the phenomena of occlusion already mentioned), the hydrated silicates and the zeolites. During dehydration these crystalline substances remain clear and transparent, and the pressure of the water vapour which they emit varies with the degree of hydration or the concentration of water in the mineral.[2] As examples of the solution of solids in solids we have the cementation of iron by charcoal, the formation of glass, and the crystallization together of isomorphous substances.

In discussing the equilibria in systems containing a solid solution, it is of essential importance to remember that a solid solution constitutes only *one* phase, a phase of varying composition, as in the case of liquid solutions.

Solution of Gases in Solids.—Comparatively little work has been done in this connection, the investigations being limited chiefly to the phenomena of occlusion or adsorption of gases by charcoal.[3] We shall, therefore, indicate only briefly and in a general manner, the behaviour which the Phase Rule enables us to foresee.[4]

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[1] Bancroft has proposed to restrict the term "occlusion" to the formation of solid solutions, and to apply "adsorption" only to effects which are primarily due to surface tension. Such a distinction, however, would probably be very difficult to carry through, for although adsorption may, in large measure, be due to surface tension, the behaviour of adsorbed substances is similar to that of substances existing in solid solutions.

[2] Tammann, *Wied. Annalen*, 1897, **63**. 16; *Zeitschr. physikal. Chem.*, 1898, **27**. 323.

[3] See, for example, Chappuis, *Wied. Annalen*, 1881, **12**. 161; Joulin, *Annal. chim. phys.* 1881, [5], **22**. 398; Kayser, *Wied. Annalen*, 1881, **12**. 526.

[4] Hoitsema, *Zeitschr. physikal. Chem.*, 1895, 17. 1.

In dealing with the systems formed by the two phases gas—olid, three chief cases call for mention:—

I. *The gas is not absorbed by the solid, but when the pressure eaches a certain value, combination of the two components can esult.*

The graphic representation of such a system is shown in Fig. 46, the ordinates being the pressures of the gas, and the abscissæ the concentrations of the gaseous component in the solid phase. Since there is no formation of a solid solution, the concentration of gas in the solid phase remains zero until the pressure has increased to the point A. At this point combination can take place. There will now be three phases present, viz. solid component, compound, and vapour. The system is therefore univariant, and if the temperature is maintained constant, the vapour pressure will be constant, irrespective of the amount of compound formed, *i.e.* irrespective of the relative amounts of gas and solid. This is shown by the line AB. When the solid component has entirely disappeared, the system ceases to be univariant, and if no absorption occurs, the pressure will increase again, as shown by BC. If a second compound can be formed, then a second *pc*-line will be obtained, similar to the preceding. To this group belong the salt hydrates (Chap. VII.).

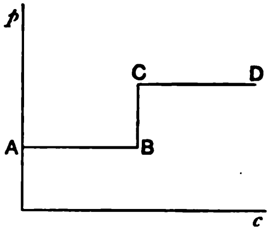

FIG. 46.

II. *The gas may be absorbed and may also form a compound.*

If absorption of gas occurs with formation of a solid solution, then, as the system consists of two phases, solution—vapour, it is bivariant. At constant temperature, therefore, the pressure will still vary with the concentration of the gaseous component in the solid phase. This is represented by the curve AB in Fig. 47. When, however, the pressure has reached a certain value, combination can take place; and since there are now three phases present, the system is univariant, and at constant temperature the pressure is constant, as shown by the line BC.

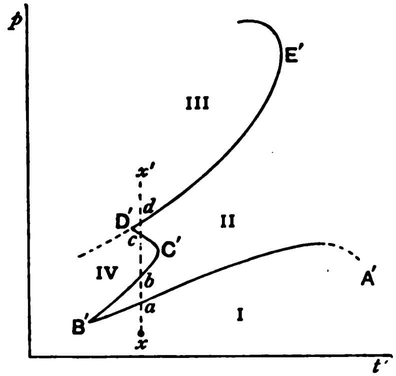

FIG. 44.

represents the pressures under which the system iodine—solution—vapour can exist, increase of volume (diminution of pressure) will cause the volatilization of the solution, and the system iodine—vapour will remain. If, therefore, we start with a system represented by *a*, diminution of pressure at constant temperature will lead to the condition represented by *x*. On the other hand, increase of pressure at *a* will lead to the condensation of a portion of the vapour phase. Since, now, the concentration of chlorine in the vapour is greater than in the solution, condensation of vapour would increase the concentration of chlorine in the solution; a certain amount of iodine must therefore pass into solution in order that the composition of the latter shall remain unchanged.[1] If, therefore, the volume of vapour be sufficiently great, continued diminution of volume will ultimately lead to the disappearance of all the iodine, and there will remain only solution and vapour (field II.). As the diminution of volume is continued, the vapour pressure and the concentration of the chlorine in the solution will increase, until when the pressure has reached the value *b*, iodine monochloride can separate out. The system, therefore, again becomes univariant, and at constant temperature the pressure and composition of the phases must remain unchanged. Diminution of volume will therefore not effect an increase of pressure, but a condensation of the vapour; and since this is richer in chlorine than the solution, solid iodine monochloride must separate out in order that the concentration of the solution remain unchanged.[1] As the result, therefore, we obtain the bivariant system iodine monochloride—vapour.

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[1] The diminution of volume is supposed to be carried out at constant temperature. The pressure and the composition of the phases must, therefore, remain unchanged, and only the relative amounts of these can undergo alteration.

A detailed discussion of the effect of a continued increase of pressure will not be necessary. From what has already been said and with the help of Fig. 44, it will readily be understood that this will lead successively to the univariant system (*c*), iodine monochloride—solution—vapour; the bivariant system solution—vapour (field II.); the univariant system (*d*), iodine trichloride—solution—vapour; and the bivariant system x', iodine trichloride—vapour. If the temperature of the experiment is above the melting point of the monochloride, then the systems in which this compound occurs will not be formed.

Sulphur Dioxide and Water.—In the case just studied we have seen that the components can combine to form definite compounds possessing stable melting points. The curves of equilibrium, therefore, resemble in their general aspect those of calcium chloride and water, or of ferric chloride and water. In the case of sulphur dioxide and water, however, the melting point of the compound formed cannot be realized, because transition to another system occurs; retroflex concentration-temperature curves are therefore not found here, but the curves exhibit breaks or sudden changes in direction at the transition points, as in the case of the systems formed by sodium sulphate and water. The case of sulphur dioxide and water is also of interest from the fact that two liquid phases can be formed.

The phases which occur are—Solid: ice, sulphur dioxide hydrate, $SO_2,7H_2O$. Liquid: two solutions, the one containing excess of sulphur dioxide, the other excess of water, and represented by the symbols $SO_2 \rightleftharpoons xH_2O$ (solution I.), and $H_2O \rightleftharpoons ySO_2$ (solution II.). Vapour: a mixture of sulphur dioxide and water vapour in varying proportions. Since there are two components, sulphur dioxide and water, the number of possible systems is considerable. Only the following, however, have been studied :—

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[1] At point *b* the ratio of chlorine to iodine in the solution is less than in the monochloride, so that by the separation of this the excess of chlorine yielded by the *condensation* of the vapour is removed.

I. *Invariant Systems : Four co-existing phases.*
  (*a*) Ice, hydrate, solution, vapour.
  (*b*) Hydrate, solution I., solution II., vapour.

II. *Univariant Systems : Three co-existing phases.*
  (*a*) Hydrate, solution I., vapour.
  (*b*) Hydrate, solution II., vapour.
  (*c*) Solution I., solution II., vapour.
  (*d*) Hydrate, solution I., solution II.
  (*e*) Hydrate, ice, vapour.
  (*f*) Ice, solution II., vapour.
  (*g*) Ice, hydrate, solution II.

III. *Bivariant Systems : Two co-existing phases.*
  (*a*) Hydrate, solution I.
  (*b*) Hydrate, solution II.
  (*c*) Hydrate, vapour.
  (*d*) Hydrate, ice.
  (*e*) Solution I., solution II.
  (*f*) Solution I., vapour.
  (*g*) Solution I., ice.
  (*h*) Solution II., vapour.
  (*i*) Solution II., ice.
  (*j*) Ice, vapour.

Pressure-Temperature Diagram.[1]—If sulphur dioxide is passed into water at 0°, a solution will be formed and the temperature at which ice can exist in equilibrium with this solution will fall more and more as the concentration of the sulphur dioxide increases. At $-2{\cdot}6°$, however, a cryohydric point is reached at which solid hydrate separates out, and the system becomes invariant. The curve AB (Fig. 45) therefore represents the pressure of the system ice—solution II.—vapour, and B represents the temperature and pressure at which the invariant system ice—hydrate—solution II.—vapour can exist. At this point the temperature is $-2{\cdot}6°$, and the pressure 21·1 cm. If heat is withdrawn from this system, the solution will ultimately solidify to a mixture of ice and hydrate, and there will be obtained the univariant system ice—hydrate—vapour. The vapour pressure of this system has been determined down to a temperature of $-9{\cdot}5^\circ$, at which temperature the pressure amounts to 15 cm. The pressures for this system are represented by the curve BC. If at the point B the volume is diminished, the pressure must remain constant, but the relative amounts of the different phases will undergo change. If suitable quantities of these are present, diminution of volume will ultimately lead to the total condensation of the vapour phase,

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[1] Roozeboom, *Rec. trav. chim.* Pays-Bas, 1884, 3. 29; 1885, 4. 65; *Zeitschr. physikal. Chem.*, 1888, 2, 450.

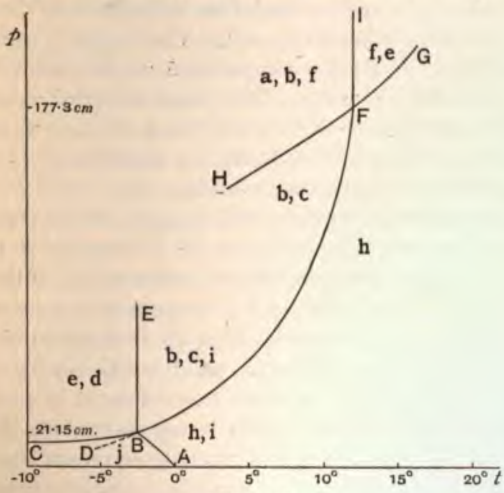

FIG. 45.

and there will remain the univariant system ice—hydrate—solution. The temperature of equilibrium of this system will alter with the pressure, but, as in the case of the melting point of a simple substance, great differences of pressure will cause only comparatively small changes in the temperature of equilibrium. The change of the cryohydric point with the pressure is epresented by the line BE; the actual values have not been letermined, but the curve must slope towards the pressure axis *ecause fusion is accompanied* by diminution of volume, as in *e case of pure ice.*

A fourth univariant system can be formed at B. This is the system hydrate—solution II.—vapour. The conditions for the existence of this system are represented by the curve BF, which may therefore be regarded as the vapour-pressure curve of the saturated solution of sulphur dioxide heptahydrate in water. Unlike the curve for iodine trichloride—solution—vapour, this curve cannot be followed to the melting point of the hydrate. Before this point is reached, a second liquid phase appears, and an invariant system consisting of hydrate—solution I.—solution II.—vapour is formed. We have here, therefore, the phenomenon of melting under the solution as in the case of succinic nitrile and water (p. 120). This point is represented in the diagram by F; the temperature at this point is 12·1°, and the pressure 177·3 cm. The range of stable existence of the hydrate is therefore from −2·6° to 12·1°; nevertheless, the curve FB has been followed down to a temperature of −6°, at which point ice formed spontaneously.

So long as the four phases hydrate, two liquid phases, and vapour are present, the condition of the system is perfectly defined. By altering the conditions, however, one of the phases can be made to disappear, and a univariant system will then be obtained. Thus, if the vapour phase is made to disappear, the univariant system solution I.—solution II.—hydrate, will be left, and the temperature at which this system is in equilibrium will vary with the pressure. This is represented by the curve FI; under a pressure of 225 atm. the temperature of equilibrium is 17·1°. Increase of pressure, therefore, raises the temperature at which the three phases can coexist.

Again, addition of heat to the invariant system at F will cause the disappearance of the solid phase, and there will be formed the univariant system solution I.—solution II.—vapour. In the case of this system the vapour pressure increases as the temperature rises, as represented by the curve FG. Such a system is analogous to the case of ether and water, or other two partially miscible liquids (p. 101). As the temperature changes, the composition of the two liquid phases will undergo change; but this system has not been studied fully.

The fourth curve, which ends at the quadruple point F, is that representing the vapour pressure of the system hydrate—solution I.—vapour (FH). This curve has been followed to a temperature of 0°, the pressure at this point being 113 cm. The metastable prolongation of GF has also been determined. Although, theoretically, this curve must lie below FH, it was found that the difference in the pressure for the two curves was within the error of experiment.

Bivariant Systems.—The different bivariant systems, consisting of two phases, which can exist within the range of temperature and pressure included in Fig. 45, were given on p. 168. The conditions under which these systems can exist are represented by the areas in the diagram, and the fields of the different bivariant systems are indicated by letters, corresponding to the letters on p. 168. Just as in the case of one-component systems (p. 27), we found that the field lying between any two curves gave the conditions of existence of that phase which was common to the two curves, so also in the case of two-component systems, a bivariant two-phase system occurs in the field enclosed[1] by the two curves to which the two phases are common. As can be seen, the same bivariant system can occur in more than one field.

As is evident from Fig. 45, three different bivariant systems are capable of existing in the area HFI; which of these will be obtained will depend on the relative masses of the different phases in the univariant or invariant system. Thus, starting with a system represented by a point on the curve HF, diminution of volume at constant temperature will cause the condensation of a portion of the vapour, which is rich in sulphur dioxide; since this would increase the concentration of sulphur dioxide in the solution, it must be counteracted by the passage of a portion of the hydrate (which is relatively poor in sulphur dioxide) into the solution. If, therefore, the amount of hydrate present is relatively very small, the final result of the compression will be the production of the system *f*, solution I.—vapour. On the other hand, if the vapour is present in relatively small amount, it will be the first phase to disappear, straight line joining the melting points of the pure compon (31·22° and 69·56°), as is evident from the following table

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[1] Two curves "enclose" a field when they form with one another an angle less than two right angles.

Molecules of bromo-cinnamic aldehyde in 100 mols. of mixture.	Freezing point.	Deviation from straight line.
0·00	31·22°	—
10·48	37·28°	2·04°
21·91	43·12°	3·50°
30·07	46·80°	4·05°
45·04	52·94°	4·45°
62·16	58·82°	3·77°
82·98	65·07°	2·03°
93·50	67·91°	0·84°
100·00	69·56°	—

Melting-point Curve.—This curve, like the freezing- curve, must also be continuous, and the melting points o different solid solutions will lie between the melting poin the pure components. This is represented by the dotted li Fig. 49, I. The relative position of the two curves, which be deduced with the help of thermodynamics and als experimental determination, is found in all cases to b accordance with the following rule: At any given tempera *the concentration of that component by the addition of whic freezing point is depressed, is greater in the liquid than in the phase*; or, conversely, *the concentration of that component addition of which the freezing point is raised, is greater i solid than in the liquid phase.* An illustration of this r afforded by the two substances chloro- and bromo-cinn aldehyde already mentioned. As can be seen from above table, the addition of chlorocinnamic aldehyde l the melting point of the bromo-compound. In accordance the rule, therefore, the concentration of the chloro-comp in the liquid phase must be greater than in the solid p and this was found experimentally. At a temperatu 49·44°, the liquid contained 58·52 per cent., the solid 52·57 per cent. of the chlorocinnamic aldehyde.

From this it will also be clear that on cooling a mixture of two substances capable of forming mixed cry the temperature of solidification will not remain constant during the separation of the solid; nor, on the other hand, will the temperature of liquefaction of the solid solution be constant. Thus, for example, if a liquid solution of two components, A and B, having the composition represented by the point x (Fig. 50), is allowed to cool, the system will pass along the line xx'. At the temperature of the point a, mixed crystals will be deposited, the composition of which will be that represented by b. As the temperature continues to fall, more and more solid will be deposited; and since the solid phase is relatively rich in the component B, the liquid will become relatively poorer in this. The composition of the liquid solution will therefore pass along the curve ad, the composition of the solid solution at the same time passing along the curve bc; at the point c the liquid will solidify completely.

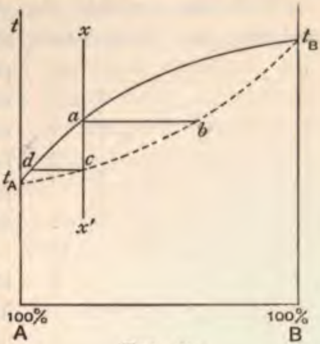

FIG. 50.

Conversely, if mixed crystals of the composition and at the temperature x' are heated, liquefaction will begin at the temperature c, yielding a liquid of the composition d. On continuing to add heat, the temperature of the mass will rise, more of the solid will melt, and the composition of the two phases will change as represented by the curves da and cb. When the temperature has risen to a, complete liquefaction will have occurred. The process of solidification or of liquefaction is therefore extended over a temperature interval ac.

Even when the freezing-point curve is a straight line joining the melting points of the pure components, the melting-point curve will not necessarily coincide with the freezing-point curve, although it may approach very near to it; complete coincidence can take place only when the melting points of the two components are identical. An example of this will be given later (Chap. XII.).

(*b*) *The freezing-point curve passes through a maximum* (Curve II., Fig. 49).

This curve exhibits the greatest degree of contrast to the freezing-point curve which is obtained when the pure components crystallize out. For, since the curve passes through a maximum, it is evident that the freezing point of each of the components must be *raised* by the addition of the other component.

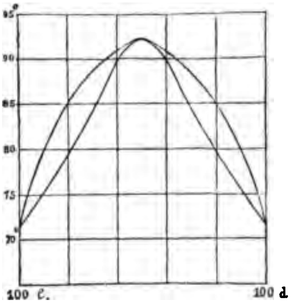

FIG. 51.

Example.—Very few cases belonging to this type are known. The best example is found in the freezing-point curve of mixtures of *d*- and *l*-carvoxime[1] ($C_{10}H_{14}N.OH$). The freezing points and melting points of the different mixtures of *d*- and *l*-carvoxime are given in the following table, and represented graphically in Fig. 51.

Per cent. of *d*-carvoxime.	Per cent. of *l*-carvoxime.	Freezing point.	Melting point.
100	0	72·0°	72·0°
99	1	72·4°	—
98	2	73·0°	—
95	5	75·4°	73·0°
90	10	79·0°	75·0°
80	20	84·6°	80·0°
70	30	88·2°	85·0°
60	40	90·4°	—
50	50	91·4°	91·4°
25	75	86·4°	82·0°
8	92	77·4°	—
1	99	72·4°	—
0	100	72·0°	72·0°

In this figure, the melting-point curve, *i.e.* the temperature-concentration curve for the mixed crystals, is represented by the lower curve. Since the addition of the lævo-form to the dextro-form raises the melting point of the latter, the concentration of the lævo-form must, in accordance with the rule given, be greater in the solid phase than in the liquid. Similarly, since addition of the dextro-form raises the melting point of the lævo-form, the solid phase must be richer in dextro- than in lævo-carvoxime. At the maximum point, the melting-point and freezing-point curves touch; at this point, therefore, the composition of the solid and liquid phases must be identical. It is evident, therefore, that at the maximum point the liquid will solidify, or the solid will liquefy completely without change of temperature; and, accordingly, mixed crystals of the composition represented by the maximum point will exhibit a definite melting point, and will in this respect behave like a simple substance.

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[1] Adriani, *Zeitschr. physikal. Chem.*, 1900, **33**. 469.

(*c*) *The freezing-point curve passes through a minimum* (Curve III., Fig. 49).

In this case, as in the case of those systems where the pure components are deposited, a minimum freezing point is obtained. In the latter case, however, there are two freezing-point curves which intersect at a eutectic point; in the case where mixed crystals are formed there is only one continuous curve. On one side of the minimum point the liquid phase contains relatively more, on the other side relatively less, of the one component than does the solid phase; while at the minimum point the composition of the two phases is the same. At this point, therefore, complete solidification or complete liquefaction will occur without change of temperature, and the mixed crystals will accordingly exhibit a definite melting point.

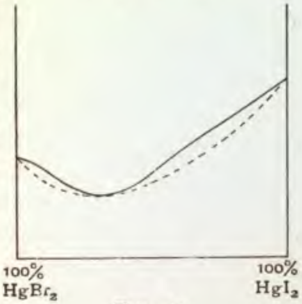

FIG. 52.

Example.—As an example of this there may be taken the mixed crystals of mercuric bromide and iodide.[1] Mercuric bromide melts at 236·5°, and mercuric iodide at 255·4°. The mixed crystal of definite constant melting point (minimum point) contains 59 mols. *per cent.* of mercuric bromide, the melting point being 216·1°.

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[1] Reinders, *Zeitschr. physikal. Chem.*, 1900, **32**, 494.

The numerical data are contained in the following tab and represented graphically in Fig. 52.

Mols. per cent. of $HgBr_2$.	Freezing point.	Melting point.
100	236·5°	236°
90	228·8°	226°
80	222·2°	219°
70	217·8°	217°
65	216·6°	216°
60	216·1°	215·5°
55	216·3°	216°
50	217·3°	216°
40	221·1°	218°
30	227·8°	223°
20	236·2°	231°
10	245·5°	242°
0	255·4°	254°

Fractional Crystallization of Mixed Crystals.—With help of the diagrams already given it will be possible to pre what will be the result of fractional crystallization fused mixture of two stances which can form mi crystals. Suppose, for ample, a fused mixture of composition x (Fig. 53 cooled down; then, as have already seen, when temperature has fallen t mixed crystals of composit b, are deposited. If the temperature is allowed to fall to x', the solid then separated from the liquid, the mixed crystal obtained will have the composition represented by e. If, i the mixed crystals e are completely fused and the fused r allowed to cool, separation of solid will occur when temperature has fallen to the point f. The mixed cry which are deposited have now the composition represente g, i.e. *they are richer in B than the original mixed crystals.* repeating this process, the composition of the successive c

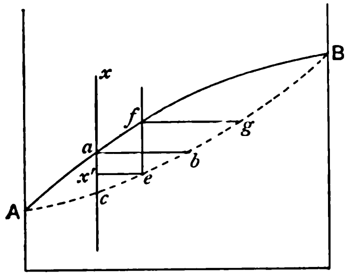

FIG. 53.

of mixed crystals which are obtained approximates more and more to that of the pure component B, while, on the other hand, the composition of the liquid phase produced tends to that of pure A. By a systematic and methodical repetition of the process of fractional crystallization, therefore, a *practically* complete separation of the components can be effected; a perfect separation is theoretically impossible.

From this it will be readily understood that in the case of substances the freezing point of which passes through a maximum, fractional crystallization will ultimately lead to mixed crystals having the composition of the maximum point, while the liquid phase will more and more assume the composition of either pure A or pure B, according as the initial composition was on the A side or the B side of the maximum point. In those cases, however, where the curves exhibit a minimum, the solid phase which separates out will ultimately be one of the pure components, while a liquid phase will finally be obtained which has the composition of the minimum point.

II.—THE TWO COMPONENTS DO NOT FORM A CONTINUOUS SERIES OF MIXED CRYSTALS.

This case corresponds to that of the partial miscibility of liquids. The solid component A can "dissolve" the component B until the concentration of the latter in the mixed crystal has reached a certain value. Addition of a further amount of B will not alter the composition of the mixed crystal, but there will be formed a second solid phase consisting of a solution of A in B. At this point the four phases, mixed crystals containing excess of A, mixed crystals containing excess of B, liquid solution, vapour, can coexist; this will therefore be an invariant point. The temperature-concentration curves will therefore no longer be continuous, but will exhibit a break or discontinuity at the point at which the invariant system is formed.

(*a*) *The freezing-point curve exhibits a transition point (Curve I, Fig. 54).*

As is evident from the figure, addition of B raises the melting point of A, and, in accordance with the rule previo given, the concentration of B in the mixed crystals will greater than in the solution. is represented in the figure by dotted curve AD. On the o hand, addition of A lowers melting point of B, and the curves BC and BE are obta for the liquid and solid pl respectively. At the temper of the line CDE the liquid tion of the composition r sented by C is in equilibrium the two different mixed cr represented by D and E. A temperature, therefore, the *te-* for the solid phase exhibits continuity ; and, since the solid phase undergoes change a point, the freezing-point curve must show a break (p. 109)

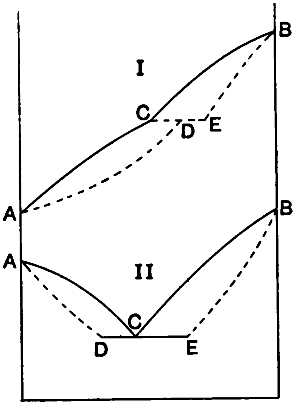

Fig. 54.

Example.—Curves of the form given in Fig. 54 I. been found experimentally in the case of silver nitrate sodium nitrate.[1] The following table contains the num data, which are also represented graphically in Fig. 55.

Molecules $NaNO_3$ per cent.	Freezing point.	Melting point.
0	208·6°	208·6°
8	211·4°	210°
15·06	215°	212°
19·46	217·2°	214·8°
21·9	222°	215°
26	228·4°	216·5°
29·7	234·8°	217·5°
36·2	244·4°	217·5°
47·3	259·4°	237·6°
58·9	272°	257°
72	284°	274°
100	308°	308°

---

[1] Hissink, *Zeitschr. physikal. Chem.*, 1900, **32**. 542.

The temperature of the transition point is 217·5°; at this point the liquid contains 19·5, and the two conjugate solid solutions 26 and 38 molecules of sodium nitrate per cent, respectively.

(*b*) *The freezing-point curve exhibits a eutectic point* (Curve II., Fig. 54).

In this case the freezing point of each of the components is lowered by the addition of the other, until at last a point is reached at which the liquid solution solidifies to a mixture or conglomerate of two mixed crystals.

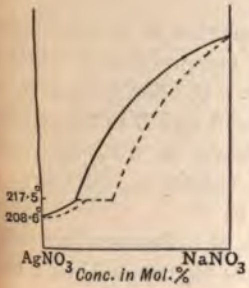

FIG. 55.

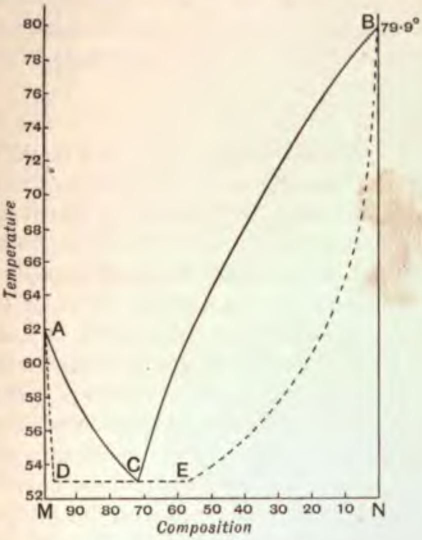

FIG. 56.

Examples.—Curves belonging to this class have been obtained in the case of potassium and thallium nitrates[1] and of naphthalene and monochloracetic acid.[2] The data for the latter are given in the following table and represented in Fig. 56.

---

[1] Van Eyk, *Zeitschr. physikal. Chem.*, 1899, **30**. 430.

[2] Cady, *Journ. Physical Chem.*, 1899, **3**. 127.

Temperature.	Liquid solution.		Solid solution.	
	Per cent. naphthalene.	Per cent. acid.	Per cent. naphthalene.	Per cent. acid.
62°	—	100	—	100
60°	4·0	96·0	1·7	98·3
55°	21·0	79·0	2·1	97·9
53·5°	29·4	70·0	—	—
55°	31·3	68·7	59·6	40·4
60°	42·4	57·6	80·3	19·7
65°	53·3	46·7	89·2	10·8
70°	69·7	32·3	95·4	4·6
75°	84·4	15·6	96·6	3·4
79·9°	100	—	100	—

At the eutectic point the liquid solution is in equilibrium with two different mixed crystals the composition of which is represented by D and E respectively. If, therefore, a fused mixture containing the two components A and B in the proportions represented by C is cooled down, it will, when the temperature has reached the point C, solidify completely to a *conglomerate* of mixed crystals, D and E.

Changes in Mixed Crystals with the Temperature.—In the case of the different types of systems represented in Fig. 49, a homogeneous liquid solution of the two components will exist at temperatures above the freezing-point curve, a homogeneous mixed crystal at temperatures below the melting-point curve, while at any point between the freezing-point and melting-point curves the mixture will separate into a solid phase and a liquid phase. In the case, however, of the two types shown in Fig. 54 the relationships are somewhat more complicated. As before, the area above the freezing-point curve gives the conditions under which homogeneous liquid solutions can exist; but below the melting-point curve two different mixed crystals can coexist. This will be best understood from Figs. 57 and 58. D and E represent, as we have seen, the composition of two mixed crystals which are in equilibrium with the liquid solution at the temperature of the point C. These two mixed crystals represent, in the one case, a saturated solution of B in A (point D), and the other a saturated solution of A in B

. Just as we saw that the mutual solubility of two
ried with the temperature, so also in the case of two
; the temperature alters, the solubility of the two solid
its in one another will change. This alteration is
diagrammatically in Figs. 57 and 58 by the dotted
ilar to the solubility curves for two mutually soluble
. 99).

se, now, that a mixed crystal of the composition *x* is
wn, it will remain unchanged until, when the temperature
allen to *t'*, the homogeneous mixed crystal breaks up
nglomerate of two mixed crystals the composition of

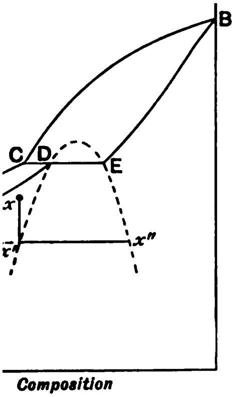

FIG. 57.

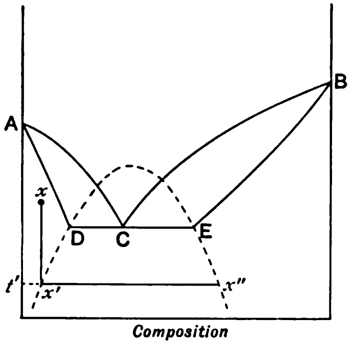

FIG. 58.

epresented by *x'* and *x''* respectively. From this, then,
seen that in the case of substances which form two solid
the mixed crystals which are deposited from the
sed mass need not remain unchanged in the solid
: may at some lower temperature lose their homo-
This fact is of considerable importance for the
of alloys.[1]

d example of this will soon be met with in the case
n and carbon alloys. The alloys of copper and tin
ish examples of the great changes which may take

---

[1] Roberts-Austen and Stansfield, *Rapports du congrès inter-*
physique, 1900, I. 363.

place in the alloy between the temperature at which it separates out from the fused mass and the ordinary temperature. Thus, for example, one of the alloys of copper and tin, which separates out from the liquid as a solid solution breaks up, on cooling, into the compound Cu_3Sn and liquid :[1] a striking example of a solid substance partially liquefying on being cooled.

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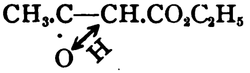
[1] Heycock and Neville, *Proc. Roy. Soc.*, 1903, **71**. 409.

CHAPTER XI

UILIBRIUM BETWEEN DYNAMIC ISOMERIDES

long been known that certain substances, *e.g.* acetoacetic re capable when in solution or in the fused state, of ; as if they possessed two different constitutions; and r to explain this behaviour the view was advanced r) that in such cases a hydrogen atom oscillated between itions in the molecule, being at one time attached to at another time to carbon, as represented by the —



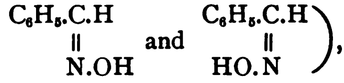
$CH_3.C—CH.CO_2C_2H_5$

ie hydrogen is in one position, the substance will act as oxy-compound; with hydrogen in the other position, tone. Substances possessing this double function are *utomeric.*

bt, however, arose as to the validity of the above tion, and this doubt was confirmed by the isolation of isomerides in the solid state, and also by the fact that city of change of the one isomeride into the other could cases be quantitatively measured. These and other ions then led to the view, in harmony with the laws of l dynamics, that tautomeric substances in the dissolved state represent a *mixture* of two isomeric forms, and iilibrium is established not by *intra-* but by *inter-* ır change, as expressed by the equation—

$$_3.CO.CH_2.CO_2C_2H_5 \rightleftarrows CH_3.C(OH):CH.CO_2C_2H_5$$

In the solid state, the one or other of the isomerides represents the stable form; but in the liquid state (solution or fusion) the stable condition is an equilibrium between the two forms.

A similar behaviour is also found in the case of other isomeric substances where the isomerism is due to difference of structure, *i.e.* structure isomerism (*e.g.* in the case of the oximes  $\begin{matrix} C_6H_5.C.H \\ \parallel \\ N.OH \end{matrix}$ and $\begin{matrix} C_6H_5.C.H \\ \parallel \\ HO.N \end{matrix}$), or to difference in configuration, *i.e.* stereoisomerism (*e.g.* optically active substances), or to polymerism (*e.g.* acetaldehyde and paraldehyde). In all such cases, although the different solid forms correspond to a single definite constitution, in the liquid state a condition of equilibrium between the two modifications is established. As a general name for these different classes of substances, the term "dynamic isomerides" has been introduced; and the different kinds of isomerism are classed together under the title "dynamic isomerism."[1]

By reason of the importance of these phenomena in the study more especially of Organic Chemistry, a brief account of the equilibrium relations exhibited by systems composed of dynamic isomerides may be given here.[2]

In studying the fusion and solidification of those substances which exhibit the relationships of dynamic isomerism, the phenomena observed will vary somewhat according as the reversible transformation of the one form into the other takes place with measurable velocity at temperatures in the neighbourhood of the melting points, or only at some higher temperature. If the transformation is very rapid, the system will behave like a one-component system, but if the isomeric change is comparatively slow, the behaviour will be that of a two-component system.

Temperature-Concentration Diagram.—The relationships which are met with here will be most readily understood with

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[1] Armstrong, *Watt's Dictionary of Chemistry* (Morley and Muir), III., p. 88. See also Lowry, *Jour. Chem. Soc.*, 1899, **75**. 211.

[2] See Bancroft, *Journ. Physical Chem.*, 1898, **2**. 143; Roozeboom, *Zeitschr. physikal. Chem.*, 1899, **28**. 288.

of Fig. 59. Suppose, in the first instance, that isomeric
mation does not take place at the temperature of the
point, then the
point curve will
simple form ACB;
rmation of com-
being for the pre-
luded. This is the
t type of curve,
es the composition
solutions in equi-
with the one modi-
(α modification) at
nt temperatures
AC); and of the

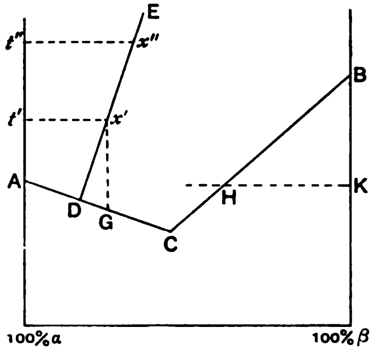

FIG. 59.

is in equilibrium with the other modification (β modi-
) at different temperatures (curve BC). C is the
point at which the two solid isomerides can exist side
in contact with the solution.

r, suppose that isomeric transformation takes place with
ble velocity. If the pure α-modification is heated to
rature t' above its melting point, and the liquid main-
at that temperature until equilibrium has been estab-
a certain amount of the β-form will be present in the
he composition of which will be represented by the
'. The same condition of equilibrium will also be
by starting with pure β. Similarly, if the tempera-
the liquid is maintained at the temperature t'', equili-
will be reached, we shall suppose, when the solution
composition x''. The curve DE, therefore, which
hrough all the different values of x corresponding to
t values of t, will represent the change of equilibrium
e temperature. It will slope to the right (as in the
if the transformation of α into β is accompanied by
on of heat; to the left if the transformation is accom-
by evolution of heat, in accordance with van't Hoff's
movable equilibrium. If transformation occurs with-
t effect, the equilibrium will be independent of the

temperature, and the equilibrium curve DE will therefore be perpendicular and parallel to the temperature axis.

We must now find the meaning of the point D. Suppose the pure α- or pure β-form heated to the temperature t', and the temperature maintained constant until the liquid has the composition x' corresponding to the equilibrium at that temperature. If the temperature is now allowed to fall sufficiently slowly so that the condition of equilibrium is continually readjusted as the temperature changes, the composition of the solution will gradually alter as represented by the curve x'D. Since D is on the freezing point curve of pure α, this form will be deposited on cooling; and since D is also on the equilibrium curve of the liquid, D is the only point at which solid can exist in stable equilibrium with the liquid phase. (The vapour phase may be omitted from consideration, as we shall suppose the experiments carried out in open vessels.) All systems consisting of the two hylotropic[1] isomeric substances α and β will, therefore, ultimately freeze at the point D, which is called the "natural" freezing point[2] of the system; provided, of course, that sufficient time is allowed for equilibrium to be established. From this it is apparent that *the stable modification at temperatures in the neighbourhood of the melting point is that which is in equilibrium with the liquid phase at the natural freezing point.*

From what has been said, it will be easy to predict what will be the behaviour of the system under different conditions. If pure α is heated, a temperature will be reached at which it will melt, but this melting point will be sharp only if the velocity of isomeric transformation is comparatively slow; *i.e.* slow in comparison with the determination of the melting point. If the substance be maintained in the fused condition for some time, a certain amount of the β modification will be formed, and on lowering the temperature the pure α form will be deposited, not at the temperature of the melting point, but at some lower temperature depending on the concentration of the β modification in the liquid phase. If isomeric transformation place slowly in comparison with the rate at which tion of the solid occurs, the liquid will become in- gly rich in the *β* modification, and the freezing point erefore, sink continuously. At the eutectic point, how- the *β* modification will also be deposited, and the ature will remain constant until all has become solid.

---

[1] Hylotropic substances are such as can undergo transformation into other substances of the same composition (Ostwald, *Lehrbuch*, II. 2. 298).

[2] Also called Equilibrium Point (Lowry).

the other hand, the velocity of transformation is ntly rapid, then as quickly as the *a* modification is ed, the equilibrium between the two isomeric forms in id phase will continuously readjust itself, and the end- f solidification will be the natural freezing point.

ilarly, starting with the pure *β* modification, the freezing fter fusion will gradually fall owing to the formation of nodification; and the composition of the liquid phase s along the curve BC. If, now, the rate of cooling is great, or if the velocity of isomeric transformation is tly rapid, complete solidification will not occur at the point; for at this temperature solid and liquid are not le equilibrium with one another. On the contrary, a quantity of the *β* modification will undergo isomeric the liquid phase will become richer in the *a* form, and zing point will *rise*; the solid phase in contact with the eing now the *a* modification. The freezing point will e to rise until the point D is reached, at which com- lidification will take place without further change of ture.

diagram also allows us to predict what will be the f rapidly cooling a fused mixture of the two isomerides. that either the *a* or the *β* modification has been main- n the fused state at the temperature t' sufficiently long ilibrium to be established. The composition of the hase will be represented by x'. If the liquid is now cooled, the composition will remain unchanged as ted by the dotted line x'G. At the temperature of the solid *a* modification will be deposited. If the cooling arried below the point G, so as to cause complete ation, the freezing point will be found to rise with time, the conversion of some of the *β* form into the *a* form in the liquid phase; and this will continue until the composition of the liquid has reached the point D. From what has just been said, it can also be seen that if the freezing point curves can be obtained by actual determination of the freezing points of different synthetic mixtures of the two isomerides, it will be possible to determine the condition of equilibrium in the fused state at any given temperature without having recourse to analysis. All that is necessary is to rapidly cool the fused mass, after equilibrium has been established, and find the freezing point at which solid is deposited; that is, find the point at which the line of constant temperature cuts the freezing point curve. The composition corresponding to this temperature gives the composition of the equilibrium mixture at the given temperature.

It will be evident, from what has gone before, that the degree of completeness with which the different curves can be realised will depend on the velocity with which isomeric change takes place, and on the rapidity with which the determinations of the freezing point can be carried out. As the two extremes we have, on the one hand, practically instantaneous transformation, and on the other, practically infinite slowness of transformation. In the former case, only one melting and freezing point will be found, viz. the natural freezing point; in the latter case, the two isomerides will behave as two perfectly independent components, and the equilibrium curve DE will not be realised.

The diagram which is obtained when isomeric transformation does not occur within measurable time at the temperature of the melting point is somewhat different from that already given in Fig. 59. In this case, the two freezing point curves AC and BC (Fig. 60) can be readily realized, as no isomeric change occurs in the liquid phase. Suppose, however, that at a higher temperature, t', reversible isomeric transformation can take place, the composition of the liquid phase will alter until at the point x' a condition of equilibrium is reached; and the composition of the liquid at higher temperatures will be represented by the curve x'F. Below the temperature t' the position of the equilibrium curve is hypothetical; but as the temperature falls the velocity of transformation diminishes, and at last becomes *practically* zero. The equilibrium curve can therefore be regarded as dividing into two branches x'G and x'H. At temperatures between G and t' the α modification can undergo isomeric change leading to a point on the curve Gx'; and the β modification can undergo change leading to a point on the curve Hx'. The same condition of equilibrium is therefore not reached from each side, and we are therefore dealing not with true but with false equilibrium (p. 5). Below the temperatures G and H, isomeric transformation does not occur in measurable time. We shall not, however, enter into a detailed discussion of the equilibria in such systems, more especially as they are not systems in true equilibrium, and as the temperature at which true equilibrium can be established with appreciable velocity alters under the influence of catalytic agents.[1] Examples of such systems will no doubt be found in the case of optically active substances, where both isomerides are apparently quite stable at the melting point. In the case of such substances, also, the action of catalytic agents in producing isomeric transformation (racemisation) is well known.

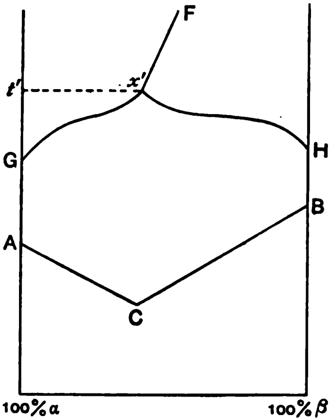

FIG. 60.

Transformation of the Unstable into the Stable Form.—As has already been stated, the stable modification in the neighbourhood of the melting point is that one which is in equilibrium with the liquid phase at the natural freezing point. In the case of polymorphic substances, we have seen (p. 37) that that form which is stable in the neighbourhood of the melting point melts at the higher temperature. That was a consequence of the fact that the two polymorphic forms on melting gave identical liquid phases. In the present case, however, the above rule does not apply, for the simple reason that the liquid phase obtained by the fusion of the one modification is not identical with that obtained by the fusion of the other. In the case of isomeric substances, therefore, the form of lower melting point *may* be the more stable; and where this behaviour is found it is a sign that the two forms are isomeric (or polymeric) and not polymorphic.[1] An example of this is found in the case of the isomeric benzaldoximes (p. 201).

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[1] For a discussion of these systems, see Roozeboom, *Zeitschr. physikal. Chem.*, *loc. cit.*

Since in Fig. 59 the α modification has been represented as the stable form, the transformation of the β into the α form will be possible at all temperatures down to the transition point. At temperatures below the eutectic point, transformation will occur without formation of a liquid phase; but at temperatures above the eutectic point liquefaction can take place. This will be more readily understood by drawing a line of constant temperature, HK, at some point between C and B. Then if the β modification is maintained for a sufficiently long time at that temperature, a certain amount of the α modification will be formed; and when the composition of the mixture has reached the point H, fusion will occur. If the temperature is maintained constant, isomeric transformation will continue to take place in the liquid phase until the equilibrium point for that temperature is reached. If this temperature is higher than the natural melting point, the mixture will remain liquid all the time; but if it is below the natural melting point, then the α modification will be deposited when the system reaches the condition represented by the point on the curve AC corresponding to the particular temperature. As isomeric transformation continues, the freezing point of the system will rise until it reaches the natural freezing point D. Similarly, if the α modification is maintained at a temperature above that of the point D, liquefaction will ultimately occur, and the system will again reach the final state represented by D.[2]

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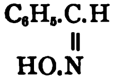
[1] See Bancroft, *loc. cit.*, p. 147; Wegscheider, *Sitzungsber. Wiener Akad.*, 1902, **110**. 908.

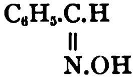
[2] Reference may be made here to the term "stability limit," introduced

Examples.—*Benzaldoximes.* The relationships which have ıst been discussed from the theoretical point of view will be endered clearer by a brief description of cases which have een experimentally investigated. The first we shall consider ; that of the two isomeric benzaldoximes:[1] —



$$\begin{array}{c} C_6H_5.C.H \\ \| \\ HO.N \end{array}$$

Benzantialdoxime (α-modification).



$$\begin{array}{c} C_6H_5.C.H \\ \| \\ N.OH \end{array}$$

Benzsynaldoxime (β-modification).

'ig. 61 gives a graphic representation of the results obtained.

The melting point of the α modification is 34–35°; the ielting point of the unstable β modification being 130°. The eezing curves AC and BC were obtained by determining ıe freezing points of different mixtures of known compo- tion, and the numbers so obtained are given in the following ble.

---

r Knorr (*Annalen*, 1896, 293. 88) to indicate that temperature above hich liquefaction and isomeric change takes place. As employed by norr and others, the term does not appear to have a very precise meaning, ıce it is used to denote, not the temperature at which these changes *can* cur, but the temperature at which the change is rapid (vide *Annalen*, 3. 91); and the introduction of an indefinite velocity of change renders e temperature of the stability limit also somewhat indefinite. The finiteness of the term is also not a little diminished by the fact that the limit" can be altered by means of catalytic agents. Since, as we have en, the stable modification *can* always undergo isomeric change and uefy at temperatures above the natural freezing point, but *not* below at point; and, further, the less stable modification can undergo isomeric insformation and liquefy at temperatures above the eutectic point, but ill not liquefy at temperatures below that; it seems to the author that it ould be more precise to identify these two points—the natural freezing int and the eutectic point—which are not altered by catalytic agents, ith the "stability limits" of the stable and unstable modification respec- vely. A perfectly definite meaning would thereby be given to the term. ı the case of those substances which do not undergo appreciable isomeric ange at the temperature of the melting point, the stability limits would the points G and H, Fig. 60.

[1] Cameron, *Journ Physical Chem.*, 1898, 2. 409.

Grams of the α modification in 100 gm. of mixture.	Freezing point.
26·2	101°
49·2	79°
73·7	46°
91·7	26·2°
95·0	28·6°
96·0	30·0°

The eutectic point C was found to lie at 25–26°, natural freezing point found to be 27·7°. Th librium curve DE was mined by heating the mixtures at different t tures until equilibriu attained, and then rapid ing the liquid. In al the freezing point was ally that of the point D. this it is seen that th librium curve must be a line parallel to the temp axis; and, therefore, i transformation in the the two benzaldoximes accompanied by any he (p. 195). This behaviour has also been found in the acetaldoxime.[1]

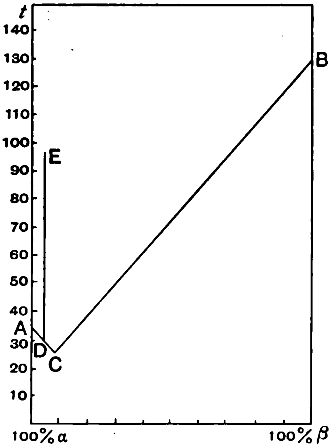


Fig. 61.

The isomeric benzaldoximes are also of interest fr fact that the stable modification has the *lower* meltin (*v.* p. 200).

Acetaldehyde and Paraldehyde.—As a second exa the equilibria between two isomerides, we shall take t isomeric (polymeric) forms of acetaldehyde, which have been exhaustively studied.[2]

---

[1] Carveth, *Journ. Physical Chem.*, 1898, **2.** 159.

[2] Hollmann, *Zeitschr. physikal. Chem.*, 1903, **43.** 129.

In the case of these two substances the reaction

$$3CH_3.CHO \rightleftarrows (CH_3.CHO)_3$$

kes place at the ordinary temperature with very great slow- ss. For this reason it is possible to determine the freezing int curves of acetaldehyde and paraldehyde. The three ief points on these curves, represented graphically in Fig. 62, :—

m.p. of acetaldehyde − 118·45°
m.p. of paraldehyde + 12·55°
eutectic point − 119·9°

order to determine the position of the natural melting point, as necessary, on account of the slowness of transformation, mploy a catalytic agent in er to increase the velocity which the equilibrium established. A drop of centrated sulphuric acid ved the purpose. In pre- ce of a trace of this sub- nce, isomeric transformation y speedily occurs, and leads he condition of equilibrium. rting in the one case with d paraldehyde, and in the er case with acetaldehyde, same freezing point, viz. 5°, was obtained, the solid ase being paraldehyde. is temperature, 6·75°, is refore the natural freezing point, and paraldehyde, the solid quilibrium with the liquid phase at this point, is the stable n.

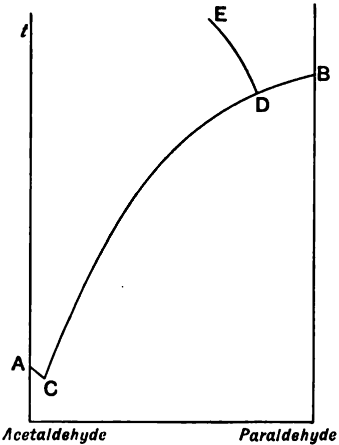


FIG. 62.

With regard to the change of equilibrium with the tempera- , it was found that whereas the liquid phase contained 11·7 lecules per cent. of acetaldehyde at the natural freezing nt, the liquid at the temperature of 41·6° contains 46·6 lecules per cent. of acetaldehyde. As the temperature rises, therefore, there is increased formation of acetaldehyde, or a decreasing amount of polymerisation. This is in harmony with the fact that the polymerisation of acetaldehyde is accompanied by evolution of heat.

While speaking of these isomerides, it may be mentioned that at the temperature 41·6° the equilibrium mixture has a vapour pressure equal to the atmospheric pressure. At this temperature, therefore, the equilibrium mixture (obtained quickly with the help of a trace of sulphuric acid) boils.[1]

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[1] For other examples of the application of the Phase Rule to isomeric substances, see *Journ. Physical Chem.*, vols. 2. *et seq.*

CHAPTER XII

SUMMARY.—APPLICATION OF THE PHASE RULE TO THE STUDY OF SYSTEMS OF TWO COMPONENTS

IN this concluding chapter on two-component systems, it is proposed to indicate briefly how the Phase Rule has been applied to the elucidation of a number of problems connected with the equilibria between two components, and how it has been employed for the interpretation of the data obtained by experiment. It is hoped that the practical value of the Phase Rule may thereby become more apparent, and its application to other cases be rendered easier.

The interest and importance of investigations into the conditions of equilibrium between two substances, lie in the determination not only of the conditions for the stable existence of the participating substances, but also of whether or not chemical action takes place between these two components; and if combination occurs, in the determination of the nature of the compounds formed and the range of their existence. In all such investigations, the Phase Rule becomes of conspicuous value on account of the fact that its principles afford, as it were, a touchstone by which the character of the system can be determined, and that from the form of the equilibrium curves obtained, conclusions can be drawn as to the nature of the interaction between the two substances. In order to exemplify the application of the principles of the Phase Rule more fully than has already been done, illustrations will be drawn from investigations on the interaction of organic compounds; on the equilibria between optically active compounds; and on alloys.

Summary of the Different Systems of Two Components.—Before passing to the consideration of the application of the Phase Rule to the investigation of particular problems, it will be well to collect together the different types of equilibrium curves with which we are already acquainted; to compare them with one another, in order that we may then employ these characteristic curves for the interpretation of the curves obtained as the result of experiment.

In investigating the equilibria between two components, three chief classes of curves will be obtained according as—

I. No combination takes place between the two components.

II. The components can form definite compounds.

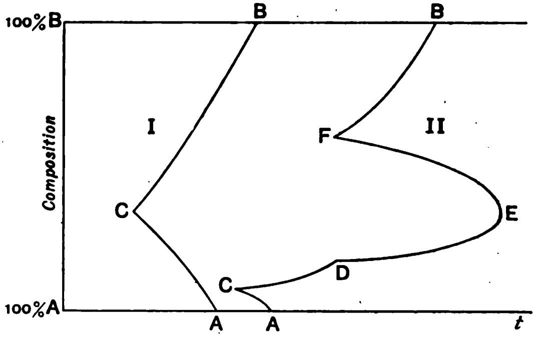

FIG. 63.

III. The components separate out in the form of mixed crystals.

The different types of curves which are obtained in these three cases are represented in Figs. 63, 64, 65. These different diagrams represent the whole series of equilibria, from the melting point of the one component (A) to that of the other component (B). The curves represent, in all cases, the composition of the solution, or phase of variable composition; the temperature being measured along one axis, and the composition along the other.

We shall now recapitulate very briefly the characteristics of the different curves.

If no compound is formed between the two components, eral form of the equilibrium curve will be that of curve ., Fig. 63. Type I. is the simplest form of curve found, sists, as the diagram shows, of only two branches, AC , meeting at the point C, *which lies below the melting either component.* The solid phase which is in equilibrium solutions AC is pure A; that in equilibrium with BC, C is the eutectic point. Although at the eutectic point tion solidifies entirely without change of temperature, d which is deposited is not a homogeneous solid phase, ixture, or conglomerate of the two components. *The point, therefore, represents the melting or freezing point, compound, but of a mixture* (p. 117).

ve II., Fig. 63, is obtained when two liquid phases are C is an eutectic point, D and F are transition points h there can co-exist the four phases—solid, two liquid vapour. DEF represents the change in the composition wo liquid phases with rise of temperature; the curve lso have the reversed ith the critical solution below the transition D and F.

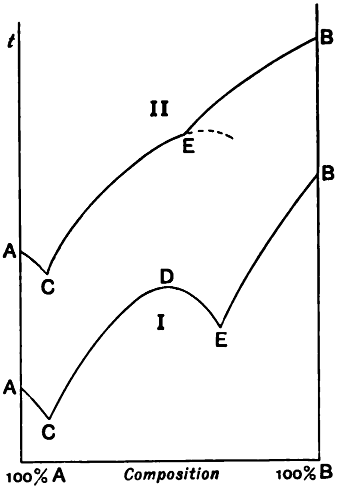

FIG. 64.

the second class of (Fig. 64), that in combination between nponents occurs, there in two types according compound formed has ite melting point (*i.e.* ist in equilibrium with ion of the same com n), or undergoes only fusion; that is, exhibits ition point.

compound possessing nite melting point is , the equilibrium curve will have the general form shown e I., Fig. 64. A, B, and D are the melting points of , pure B, and of the compound A_xB_y respectively. AC is the freezing point curve of A in presence of B; BE that of B in presence of A; and DC and DE the freezing point curves of the compound in presence of a solution containing excess of one of the components. C and E are eutectic points at which mixtures of A and A_xB_y, or B and A_xB_y, can co-exist in contact with solution. The curve CDE may be large or small, and the melting point of the compound, D, may lie above or below that of each of the components, or may have an intermediate position. If more than one compound can be formed, a series of curves similar to CDE will be obtained (*cf.* p. 149).

On the other hand, if the compound undergoes transition to another solid phase at a temperature below its melting point, a curve of the form II., Fig. 64, will be found. This corresponds to the case where a compound can exist only in contact with solutions containing excess of one of the components. The metastable continuation of the equilibrium curve for the compound is indicated by the dotted line, the summit of which would be the melting point of the compound. Before this temperature is reached, however, the solid compound ceases to be able to exist in contact with solution, and transition to a different solid phase occurs at the point E (*cf.* p. 132). This point, therefore, represents the limit of the existence of the compound AB. If a series of compounds can be formed none of which possess a definite melting point, then a series of curves will be obtained which do not exhibit a temperature-maximum, and there will be only one eutectic point. The limits of existence of each compound will be marked by a break in the curve (*cf.* p. 141).

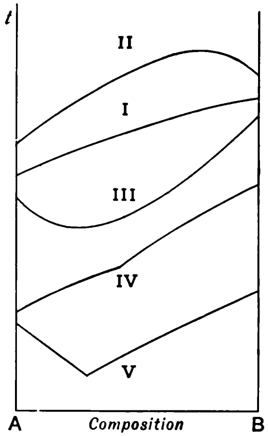

FIG. 65.

Turning, lastly, to the third class of systems, in which formation of mixed crystals can occur, five different types of curves can be obtained, as shown in Fig. 65. With regard to the first three types, curves I., II., and III., hese differ entirely from those of the previous classes, in that hey are continuous; they exhibit no eutectic point, and no ransition point. Curve II. bears some resemblance to the nelting-point curve of a compound (*e.g.* CDE, Fig. 64, I.), but differs markedly from it in not ending in eutectic points.

Further, in the case of the formation of a compound, the composition of the solid phase remains unchanged throughout the whole curve between the eutectic points; whereas, when mixed crystals are produced, the composition of the solid phase varies with the composition of the liquid solution. On passing through the maximum, the relative proportions of A and B in the solid and the liquid phase undergo change; on the one side of the maximum, the solid phase contains relatively more A, and on the other side of the maximum, relatively more B than the liquid phase. Lastly, when mixed crystals are formed, the temperature at which complete solidification occurs changes as the composition of the solution changes, whereas in the case of the formation of compounds, the temperature of complete solidification for all solutions is a eutectic point.

The third type of curve, Fig. 65, can be distinguished in a similar manner from the ordinary eutectic curve, Fig. 63, I., to which it bears a certain resemblance. Whereas in the case of the latter, the eutectic point is the temperature of complete solidification of all solutions, the point of minimum temperature in the case of the formation of mixed crystals, is the solidification point only of solutions having one particular composition; that, namely, of the minimum point. For all other solutions, the temperature of complete solidification is different. Whereas, also, in the case of the simple eutectic curve, the solid which separates out from the solutions represented by either curve remains the same throughout the whole extent of that curve, the composition of the mixed crystal varies with variation of the composition of the liquid phase, and the relative proportions of the two components in the solid and the liquid phase are reversed on passing through the minimum.[1]

In a similar manner, type IV., Fig. 65, can be distinguished *from type II., Fig. 64,* by the fact that it does not exhibit a eutectic point, and that the composition of the solid phase undergoes continuous variation with variation of the liquid phase on either side of the transition point. Lastly, type V., which does exhibit a eutectic point, differs from the eutectic curve of Fig. 63, in that the eutectic point does not constitute the point of complete solidification for all solutions, and that the composition of the solid phase varies with the composition of the liquid phase.

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[1] *See Roozeboom, Zeitschr. physikal. Chem.*, 1899, 30. 410.

Such, then, are the chief general types of equilibrium curves for two-components; they are the pattern curves with which other curves, experimentally determined, can be compared; and from the comparison it will be possible to draw conclusions as to the nature of the equilibria between the two components under investigation.

1. *Organic Compounds.*

The principles of the Phase Rule have been applied to the investigation of the equilibria between organic compounds, and

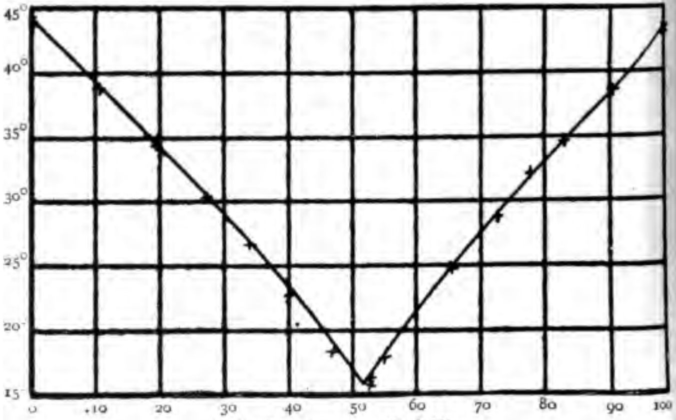

FIG. 66.

Figs. 66–69 reproduce some of the results which have been obtained.

Fig. 66, the freezing point curve (curve of equilibrium) for *o*-nitrophenol and *p*-toluidine, shows a curve of the simplest type[1] (type I., Fig. 63), in which two branches meet at an eutectic point. The solid phase in equilibrium with solutions epresented by the left-hand branch of the curve was *o*-nitrophenol (m.p. 44·1°); that in equilibrium with the solutions epresented by the right-hand branch, was *p*-toluidine (m.p. 3·3°). At the eutectic point (15·6°), these two solid phases ould co-exist with the liquid phase. This equilibrium curve, herefore, shows that *o*-nitrophenol and *p*-toluidine do not ombine with one another.

In connection with this curve, attention may be called to he interesting fact that although the solid produced by cooling he liquid phase at the eutectic point has a composition approximating to that of a compound of equimolecular proportions of he phenol and toluidine, and a constant melting point, it is evertheless a *mixture*. Although, as a rule, the constituents f the eutectic mixture are not present in simple molecular roportions, there is no reason why they should not be so; and t is therefore necessary to beware of assuming the formation f compounds in such cases.[2]

Fig. 67, on the other hand, indicates with perfect ertainty the formation of a compound between phenol and -naphthylamine.[3] (*Cf.* curve I., Fig. 64.)

Phenol freezes at 40·4°, but the addition of α-naphthylamine owers the freezing point as represented by the curve AC. At C (16·0°) the compound $C_6H_5OH,C_{10}H_7NH_2$ is formed, and the ystem becomes invariant. On increasing the amount of the mine, the temperature of equilibrium rises, the solid phase ow being the compound. At D, the curve passes through a aximum (28·8°), at which the solid and liquid phases have he same composition. This is the melting point of the compound. Further addition of the amine lowers the temperature f equilibrium, until at E solid α-naphthylamine separates out, nd a second eutectic point (24·0°) is obtained. BE is the freezing-point curve of α-naphthylamine in presence of phenol, the freezing point of the pure amine being 48·3°.

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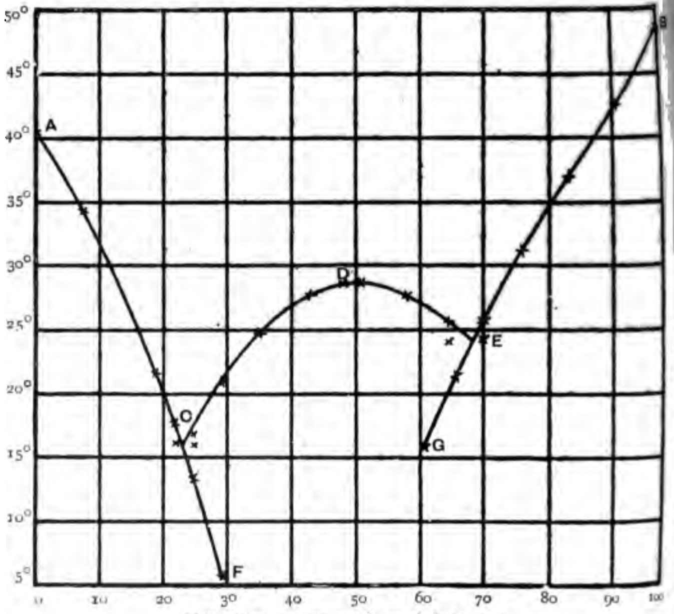
[1] J. C. Philip, *Journ. Chem. Soc.*, 1903, **83**. 821.

[2] *Cf.* also Paterno and Ampolla, *Gazzetta chim. ital.*, 1897, **27**. 481.

[3] Philip, *loc. cit.*, p. 826.

On account of the great sluggishness with which the compound of phenol and α-naphthylamine crystallizes, it was found possible to follow the freezing point curves of phenol and the amine to temperatures considerably below the eutectic points, as shown by the curves CF and EG.



Molecular percentage of α-naphthylamine.

FIG. 67.

Phenol can also combine with *p*-toluidine in equimolecular proportions; and this compound is of interest, from the fact that it exists in two crystalline forms melting at 28·5° and 30°. Each of these forms now must have its own equilibrium curve, and it was found that the intermediate portion of the freezing point curve was duplicated, as shown in Fig. 68.[1]

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[1] Philip, *loc. cit.*, p. 829. Compare curves for iodine monochloride, Fig. 42, p. 160.

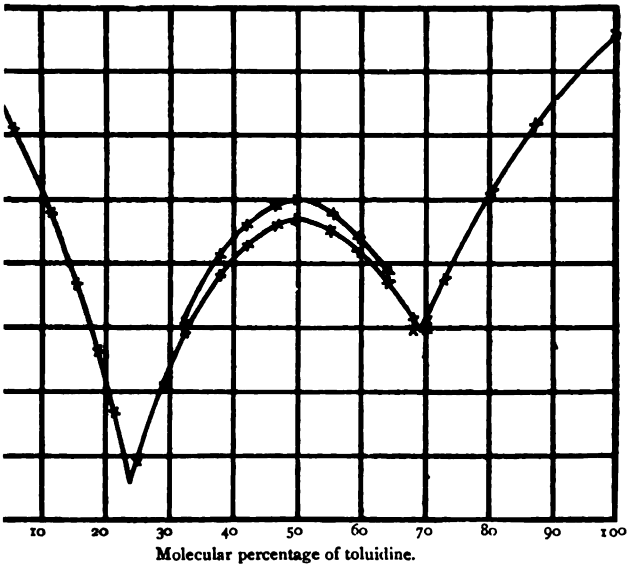
10
20
30
40
50
60
70
80
90
100
Molecular percentage of toluidine.

FIG. 68.

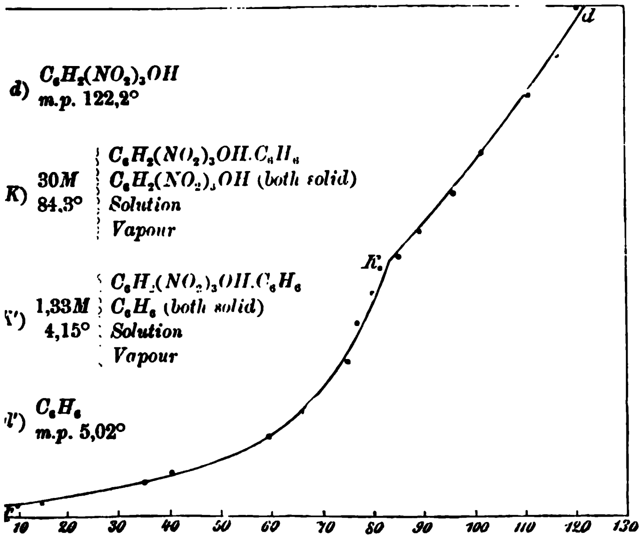
d
d) $C_6H_2(NO_2)_3OH$
m.p. 122,2°
K) 30M
84.3°
$C_6H_2(NO_2)_3OH.C_6H_6$
$C_6H_2(NO_2)_3OH$ (both solid)
Solution
Vapour
K
') 1,33M
4,15°
$C_6H_2(NO_2)_3OH.C_6H_6$
C_6H_6 (both solid)
Solution
Vapour
') C_6H_6
m.p. 5,02°
E
10
20
30
40
50
60
70
80
90
100
110
120
130

FIG. 69.

Lastly, a curve is given, Fig. 69,[1] which corresponds with curve II., Fig. 64. Picric acid and benzene can form a compound, which, however, can exist only in contact with solutions *containing excess of benzene*. When the temperature is raised, a point (K) is reached at which the compound melts with separation of solid picric acid. The point, K, is, therefore, a *transition point;* analysis, however, showed that the composition of the solution at this point is very nearly that of the compound $C_6H_2(NO_2)_3OH,C_6H_6$, so that the melting point of the compound can almost be reached. The fusion of the compound of benzene and picric acid with separation of the latter is analogous to the (partial) fusion of Glauber's salt with separation of anhydrous sodium sulphate.

2. *Optically Active Substances.*

The question as to whether a resolvable inactive body is a mixture of the two oppositely active constituents (a *dl*-mixture), or a racemic compound, is one which has given rise to considerable discussion during the past decade; and several investigators have endeavoured to establish general rules by which the question could be decided. In the case of inactive liquids it is a matter of great difficulty to arrive at a certain conclusion as to whether one is dealing with a mixture or a compound, for in this case the usual physical methods give but a dubious answer; and although the existence of a racemate in the liquid state (in the case of conine) has been asserted,[2] most chemists incline to the belief that such a thing is improbable.

Even in the case of crystalline substances, where the differences between the various forms is greater, it was not always easy to discriminate between the *dl*-mixture and the racemic compound. The occurrence of hemihedral faces was considered by Pasteur to be a sufficient criterion for an optically active substance. It has, however, been found that hemihedry in crystals, although a frequent accompaniment of optical activity, is by no means a necessary or constant expression of this property. Other rules, also, which were given, although in some cases reliable, were in other cases insufficient; and all were in so far unsatisfactory that they lacked a theoretical basis.

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[1] Kuriloff, *Zeitschr. physikal. Chem.*, 1897, **23**. 676.

[2] Ladenburg, *Ber.*, 1895, **28**. 163; 1991.

With the help of the Phase Rule, however, it is possible from a study of the solubility or fusion curves of the optically active and inactive substances, to decide the nature of the inactive substance, at least under certain conditions. On account of the interest and importance which these compounds possess, a brief description of the application of the Phase Rule to the study of such substances will be given here;[1] the two optical antipodes being regarded as the two components.

In the present chapter we shall consider only the fusion curves, the solubility curves being discussed in the next section on three-component systems. The rules which are hereby obtained, have reference only to the nature of the inactive substance in the neighbourhood of the melting points.

I. *The inactive substance is a* dl-*mixture.*

In this case the fusion curves will have the simple form shown in type I., Fig. 63. A and B are the melting points of the two optical isomerides, and C the eutectic point at which the inactive mixture consisting of equal amounts of d- and l- form melts. Owing to the similar effect of the one form on the freezing point of the other, the figure is symmetrical. No example of this simple case has been investigated.

II. *The two components form a racemic compound.*

In this case there will be three melting point curves as in Fig. 64, type I. In this case also the figure must be symmetrical.

Examples.—As examples of this, may be taken dimethyl tartrate and mandelic acid, the freezing point curves of which are given in Figs. 70 and 71.[2] As can be seen, the curve for the racemic tartrate occupies a large part of the diagram, while that for racemic mandelic acid is much smaller. In the case of dimethyldiacetyl tartrate, this middle portion is still less.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1899, **28**. 494; Adriani, ibid., *1900,* **33**. *453.*

[2] *Adriani, Zeitschr. physikal. Chem.*, 1900, **33**. 453.

Active dimethyl tartrate melts at 43·3°; racemic dimethyl tartrate at 89·4°. Active mandelic acid melts at 132·8°; the racemic acid at 118·0°. In the one case, therefore, the racemic compound has a higher, in the other a lower melting point than the active forms.

In the case of partially racemic compounds (*i.e.* the compound of a racemate with an optically active substance) the type of curve will be the same, but the figure will no longer be symmetrical.

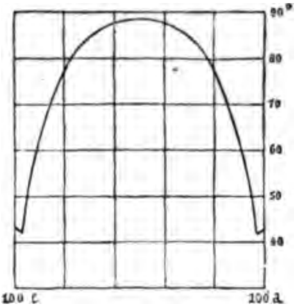

FIG. 70.

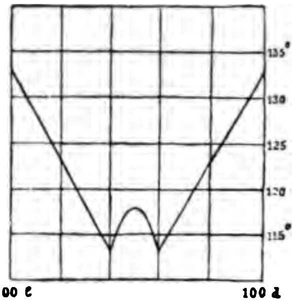

FIG. 71.

III. *The inactive substance is a pseudo-racemic mixed crystal.* In cases where the active components can form mixed crystals, the freezing point curve will exhibit one of the forms given in Fig. 65. The inactive mixed crystal containing 50 per cent. of the dextro and laevo compound, is known as a pseudo-racemic mixed crystal.[1] So far, only curves of the types I. and II. have been obtained.

Examples.—The two active camphor oximes are of interest from the fact that they form a continuous series of mixed crystals, *all of which have the same melting point.* The cur which is obtained in this case is, therefore, a straight lin *joining* the melting points of the pure active components; th

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[1] Kipping and Pope, *Journ. Chem. Soc.*, 1897, 71. 993.

: of the active isomerides and of the whole series stals being 118·8°.

ase of the carvoximes mixed crystals are also the equilibrium curve in this case exhibits a ig. 72). At this maxi- ie composition of the the liquid solution is since the curve must ical, this maximum cur in the case of the aining 50 per cent. of ent, which will there- ctive. Further, this ed crystal will melt at the same tempera- iave, therefore, like a ipound (p. 185). The melting point of the active s 72°; that of the inactive pseudo-racemic mixed 4°.

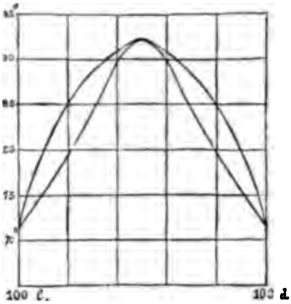

FIG. 72.

nations.—As has already been remarked, the which can be drawn from the fusion curves regard- e of the inactive substances formed hold only for in the neighbourhood of the melting points. At below the melting point transformation may occur; te may break up into a *dl*-mixture, or a pseudo- ed crystal may form a racemic compound. We later point meet with examples of a racemic hanging into a *dl*-mixture at a definite transition he pseudo-racemic mixed crystal of camphoroxime ple of the second transformation. Although at in the neighbourhood of the melting point the amphoroximes form only mixed crystals but no a racemic compound is formed at temperatures At this temperature the inactive pseudo-racemic l changes into a racemic compound; and in the other mixed crystals transformation to racemate of) active component also occurs, although at a erature than in the case of the inactive mix crystal. Although this behaviour is one of considera importance, this brief reference to it must suffice here.[1]

3. *Alloys.*

One of the most important classes of substances in study of which the Phase Rule has been of very conside importance, is that formed by the mixtures or compoun metals with one another known as alloys. Although i investigation of the nature of these bodies various metho employed, one of the most important is the determinati the character of the freezing point curve; for from the fc this, valuable information can, as we have already learn obtained regarding the nature of the solid substances separate out from the molten mixture.

Although it is impossible here to discuss fully the e mental results and the oftentimes very complicated relatio which the study of the alloys has brought to light, a reference to these bodies will be advisable on accoun of the scientific interest and of the industrial impc attaching to them.[2]

We have already seen that there are three chief ty freezing point curves in systems of two components, viz obtained when (1) the pure components crystallize ou the molten mass; (2) the components form one or compounds; (3) the components form mixed crystals. case of the metals, representatives of these three class also found.

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[1] See Roozeboom, *Zeitschr. physikal. Chem.*, 1899, **28**. 512; *ibid.*, 1900, **33**. 473; 1901, **36**. 168.

[2] In this connection reference should be made more especiall paper by Roberts-Austen and Stansfield, "Sur la constitution des métalliques," in the *Rapports du congrès international de physique*, 363; J. A. Mathews, *Journ. of the Franklin Inst.*, 1902; Gautier, *rend.*, 1896, **123**. 109; Roberts-Austen, "Reports of the Alloys F Committee," in *Journ. Inst. Mechan. Engineers*, from 1891 to 1902; papers by Heycock and Neville, published in the *Journ. Chem. S* the *Trans. Roy. Soc.* since 1897; also Neville, *Reports of the* *intion*, 1900, p. 131.

'e components separate out in the pure state.

s case the freezing point curve is of the simple type,
. Such curves have been obtained in the case of a
pairs of metals, *e.g.* zinc—cadmium, zinc—aluminium,
silver (Heycock and Neville), tin—zinc, bismuth—
itier), and in other cases. From molten mixtures
d by one branch of the freezing point curve one of
s will be deposited; while from mixtures represented
ier branch, the other metal will separate out. At the
oint the molten mass will solidify to a *heterogeneous*
f the two metals, forming what is known as the *eutectic*
ich an alloy, therefore, will melt at a definite tempera-
than the melting point of either of the pure metals.
following table are given the temperature and the
on of the liquid at the eutectic point, for three pairs
—

	Temperature.	Composition of liquid.
ium . .	264·5°	73·5 atoms per cent. of cadmium.
nium . .	380·5°	11 ,, ,, aluminium.
ver . .	778°	40 ,, ,, copper.

nelting points of the pure metals are, zinc, 419°;
322°; silver, 960°;
081°; aluminium, 650°.
e two metals can form one
mpounds.

s case there will be ob-
t only the freezing-point
he pure metals, but each
l formed will have its
ing-point curve, exhibit-
it of maximum tempera-
ending on either side in
c point. The simplest
this type will be ob-
n only one compound is formed, as is the case with

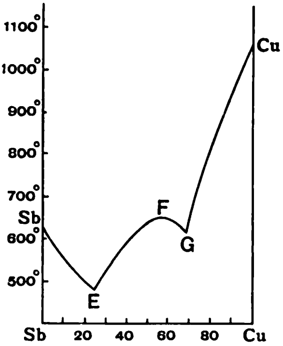

FIG. 73.

antimony and copper.[1] This curve is given in Fig. 73, where the summit of the intermediate curve corresponds with a composition Cu_2Sb or Cu_6Sb_2. Similar curves are also given by nickel and tin, by aluminium and silver, and by other metals, the formation of definite compounds between these pairs of metals being thereby indicated.[2]

A curve belonging to the same type but more complicated is obtained with gold and aluminium;[3] in this case, several compounds are formed, some of which have a definite melting point, while others exhibit only a transition point. The chief compound is $AuAl_2$, which has practically the same melting point as pure gold.

3. *The two metals form mixed crystals (solid solutions).*

The simplest case in which the metals crystallize out together is found in silver and gold.[4] The freezing point curve in this case is an almost straight line joining the freezing points of the pure metals (*cf.* curve I., Fig. 65, p. 208). These two metals, therefore, can form an unbroken series of mixed crystals.

In some cases, however, the two metals do not form an unbroken series of mixed crystals. In the case of zinc and silver,[5] for example, the addition of silver *raises* the freezing point of the mixture, until a transition point is reached. This corresponds with curve IV., Fig. 65. Silver and copper, and gold and copper on the other hand, do not form unbroken series of mixed crystals, but the freezing point curve exhibits an eutectic point, as in curve V., Fig. 65.

Not only may there be these three different types of curves, but there may also be combinations of these. Thus the two metals may not only form compounds, but one of the metals may not separate out in the pure state at all, but form mixed crystals. In this case the freezing point may rise (as in the se of silver and zinc), and one of the eutectic points will be sent.

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[1] Le Chatelier, *Revue Générale des Sciences*, 1895, **12**. 537 ; or *Bull. Soc. d'Encouragement*, 1895 [4], **10**. 573.

[2] Gautier, *Bull. Soc. d'Encouragement*, 1896 [5], **1**. 1312.

[3] Heycock and Neville, *Phil. Trans.*, 1900, **194**. 201.

[4] Gautier, *loc. cit.*

[5] Heycock and Neville, *Journ. Chem. Soc.*, 1897, **71**. 414.

Iron—Carbon Alloys.—Of all the different binary alloys, robably the most important are those formed by iron and arbon; alloys consisting not of two metals but of a metal and non-metal. On account of the importance of these alloys, an ttempt will be made here to describe in brief some of the most mportant relationships met with; dealing only with those portions of the very complicated subject about which there is practical certainty.

Before proceeding to discuss the applications of the Phase Rule to the study of the iron—carbon alloys, however, the main facts with which we have to deal may be stated very briefly. With regard to the metal itself, it is known to exist in three different allotropic modifications, called α-, β-, and γ-*ferrite* respectively. Of these, we shall consider only the first two. Like the two modifications of sulphur or of tin, α- and β-ferrite exhibit a transition point, at which the relative stability of the two forms changes. This transition point lies at 850°; and below this temperature the α-form, above this temperature the β-form is stable. These two forms of iron, further, possess different properties. Thus β-ferrite, the stable form above 850°, is non-magnetic, and has the property of dissolving carbon so as to form a homogeneous solid solution. α-Ferrite, on the other hand, is magnetic, and does not possess the property of dissolving carbon. It corresponds practically to the purest wrought iron.

Various alloys of iron and carbon, also, have to be distinguished. First of all, there is *hard steel*, containing various amounts of carbon up to 2 per cent. Microscopic examination shows that these mixtures, in spite of the varying amount of carbon, are all homogeneous; and they are therefore to be regarded as *solid solutions*. To these the name *martensite* is also given. *Perlite* contains about 0·8 per cent. of carbon; on microscopic examination, this is found to be a heterogeneous mixture. If heated above a certain temperature, perlite becomes homogeneous, and forms martensite. Lastly, there is a definite *compound* of iron and carbon called *cementite*, having he formula Fe_3C.

A short description may now be given of the application of the Phase Rule to the two-component system iron—carbon; and of the diagram showing how the different systems are related, and with the help of which the behaviour of the different mixtures under given conditions can be predicted. This diagram is shown in Fig. 74.[1]

The curve AC is the freezing-point curve for iron, BC the unknown freezing point curve for graphite. C is an eutectic point. Suppose, now, that we start with a mixture of iron and carbon represented by the point *x*. On lowering the temperature, a point, *y*, will be reached at which solid begins to separate out. This solid phase, however, is not pure iron, but a solid solution of iron and carbon having the composition represented by *y'* (*cf.* p. 183). As the temperature continues to fall, the composition of the liquid phase changes in the direction *y*C, while the composition of the solid which separates

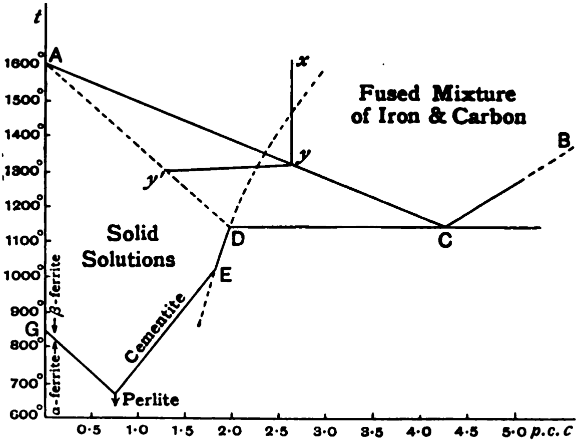

FIG. 74.

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[1] See Roberts-Austen, *Introduction to Metallurgy*, 5th edit., p. 102; Bakhuis Roozeboom, *Journ. Iron and Steel Inst.*, 1900, II. 311; *Zeitschr. physikal. Chem.*, 1900, **34**. 437; von Jüptner, *Siderology*, p. 223 (translation by C. Salter); van't Hoff, *Zinn*, Gips, und Stahl, p. 24, or Acht Vorträge *über physikalische Chemie*, p. 37.

out changes in the direction y'D; and, finally, when the composition of the molten mass is that of the point C (4·3 per cent. carbon), the whole mass solidifies to a heterogeneous mixture of two solid solutions, one of which is represented by D (containing 2 per cent. of carbon), while the other will consist practically of pure graphite, and is not shown in the figure. The temperature of the eutectic point is 1130°.

Even below the solidification point, however, changes can take place. As has been said, the solid phase which separates out from the molten mass is a solid solution represented by the point D; and the curve DE represents the change in the composition of this solid solution with the temperature. As indicated in the figure, DE forms a part of a curve representing the mutual solubility of graphite in iron and iron in graphite; the latter solutions, however, not being shown, as they would lie far outside the diagram. As the temperature falls, therefore, below 1130°, more and more graphite separates out, until at E, when the temperature is 1000°, the solid solution contains only 1·8 per cent. of carbon. At this temperature, also, cementite begins to separate out, and continues to separate out from the solid solution as the temperature falls, until at F, 670°, an eutectic point is reached, at which pure iron, α-ferrite, also appears. At the point F the solid solution contains 0·8 per cent. of carbon, so that at F an alloy of perfectly definite composition is formed, consisting of a heterogeneous mixture of α-ferrite and cementite. This constitutes perlite. The curve GF, finally, represents the composition of the solid solutions from which pure α-ferrite separates out.

As is evident, the iron—carbon mixtures furnish a splendid example of changes taking place in solid solutions which are completely analogous to those occurring in liquid solutions. A marked difference is, however, observed in that transformation occurs with very much greater slowness; as was, indeed, to be expected.

It might not be amiss to go over the curves once more, but in the *reverse direction*, noticing as we go analogies to other *systems we have studied*. First of all, G, the transition point of α-ferrite to β-ferrite is analogous to a freezing point; and, like a freezing point, it is lowered by the presence of a second substance. In this way the curve GF is obtained, which is therefore analogous to a freezing point curve; the point F corresponding with a cryohydric point, at which iron and the compound cementite exist together. We have, therefore, a system precisely similar to that found at the cryohydric point of a salt hydrate. The curve FE, now, will correspond with the solubility curve of the salt hydrate, E being a transition point at which the compound breaks up into two solid solutions. This transition point, therefore, would be analogous to the point at which a solid melts under the solvent and yields two liquid phases (*e.g.* succinic nitrile and water; p. 120).

Before concluding this brief account, let us examine the behaviour of certain mixtures under given conditions. Let us start, say, with a solid solution of carbon in iron containing less than 0·8 per cent. of carbon, at a temperature of 900°. At this temperature of course the mass is solid. On slowly cooling down this mixture, a point will be reached at which α-ferrite begins to separate out, so that the remaining homogeneous solid solution becomes richer in carbon. This process goes on until the point F (670°) is reached, when the mass separates out into a mixture of ferrite and cementite. If the original solid solution contained 0·8 per cent. of carbon, we should reach the temperature of 670° without any change taking place in the mass; and at this temperature the homogeneous mass would then break up into a heterogeneous mixture of ferrite and cementite, constituting perlite. Similarly, with solutions containing between 0·8 and 1·8 per cent. of carbon; cementite would first separate out from the homogeneous solid solution. All solid solutions, therefore, containing up to 1·8 per cent. of carbon yield, on slow cooling, heterogeneous mixtures which constitute soft steels or, when the carbon content is small, wrought iron.

The case, however, is different if the solid solution of carbon in iron is *rapidly* cooled from a temperature above the curve GFE to a temperature below this curve. In this case, the rapid cooling does not allow time for the various changes which have just been described to take place; so that the homogeneous solid solution on being rapidly cooled (chilled) remains homogeneous. In this way hard steel is obtained. By varying the rapidity of cooling, as is done in the tempering of steel, varying degrees of hardness can be obtained.

CHAPTER XIII

SYSTEMS OF THREE COMPONENTS

General.—It has already been made evident that an increase in the number of the components from one to two gives rise to a considerable increase in the possible number of systems, and introduces not a few complications into the equilibrium relations of these. No less is this the case when the number of components increases from two to three; and although examples of all the possible types of systems of three components have not been investigated, nor, indeed, any one type fully, nevertheless, among the systems which have been studied experimentally, cases occur which not only possess a high scientific interest, but are also of great industrial importance. On account not only of the number, but more especially of the complexity of the systems constituted of three components, no attempt will be made to give a full account, or, indeed, even a survey of all the cases which have been subjected to a more or less complete experimental investigation; on the contrary, only a few of the more important classes will be selected, and the most important points in connection with the behaviour of these described.

On applying the Phase Rule

$$P + F = C + 2$$

to the systems of three components, we see that in order that the system shall be invariant, no fewer than five phases must be present together, and an invariant system will therefore exist at a *quintuple* point. Since the number of liquid phases can never exceed the number of the components, and since there can be only one vapour phase, it is evident that in this case, in others, there must always be at least one solid phase sent at the quintuple point. As the number of phases ninishes, the variability of the system can increase from one four, so that in the last case the condition of the system will t be completely defined until not only the temperature and total pressure of the system, but also the concentrations of o of the components have been fixed. Or, instead of the ncentrations, the partial pressures of the components may o be taken as independent variables.

Graphic Representation.—Hitherto the concentrations of components have been represented by means of rectangular -ordinates, although the numerical relationships have been pressed in two different ways. In the one case, the concentition of the one component was expressed in terms of a fixed ount of the other component. Thus, the solubility of a salt s expressed by the number of grams of salt dissolved by 100 ams of water or other solvent; and the numbers so obtained re measured along one of the co-ordinates. The second ordinate was then employed to indicate the change of other independent variable, *e.g.* temperature. In the other se, the combined weights of the two components A and B re put equal to unity, and the concentration of the one pressed as a fraction of the whole amount. This method ows of the representation of the complete series of concentions, from pure A to pure B, and was employed, for ample, in the graphic representation of the freezing point rves.

Even in the case of three components rectangular codinates can also be employed, and, indeed, are the most venient in those cases where the behaviour of two of the nponents to one another is very different from their aviour to the third component; as, for example, in the case two salts and water. In these cases, the composition of the tem can be represented by measuring the amounts of each the two components in a given weight of the third, along co-ordinates at right angles to one another; and the change the system with the temperature can then be represented by hird axis at right angles to the first two. In those cases, however, where the three components behave in much the same manner towards one another, the rectangular co-ordinates are not at all suitable, and instead of these a *triangular diagram* is employed. Various methods have been proposed for the graphic representation of systems of three components by means of a triangle, but only two of these have been employed to any considerable extent; and a short description of these two methods will therefore suffice.[1]

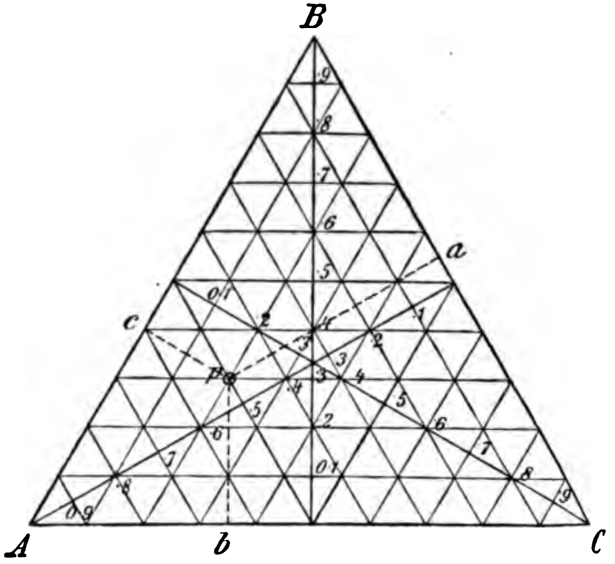

FIG. 75.

In the method proposed by Gibbs an equilateral triangle of unit height is used (Fig 75).[2] The quantities of the different components are expressed as fractional parts of the whole, and the sum of their concentrations is therefore equal to unity, and can be represented by the height of the triangle. The corners f the triangle represent the pure substances A, B, and C espectively. A point on one of the sides of the triangle will give the composition of a mixture in which only two components are present, while a point within the triangle will represent the composition of a ternary mixture. Since every point within the triangle has the property that the sum of the perpendiculars from that point on the sides of the triangle is equal to unity (the height of the triangle), it is evident that the composition of a ternary mixture can be represented by fixing a point within the triangle such that the lengths of the *perpendiculars* from the point to the sides of the triangle are equal respectively to the fractional amounts of the three components present; the fractional amount of A, B, or C being represented by the perpendicular distance from the side of the triangle *opposite* the corners A, B, and C respectively.

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[1] G. G. Stokes, *Proc. Roy. Soc.*, 1891, **49.** 174; Gibbs, *Trans. Conn. Acad.*, 1876, **3.** 176; Roozeboom, Zeitschr. physikal. *Chem.*, 1894, **15.** 147.

[2] This figure has been taken from Ostwald's Lehrbuch, II. 2. 984.

The location of this point is simplified by dividing the normals from each of the corners on the opposite side into ten or one hundred parts, and drawing through these divisions lines at right angles to the normal and parallel to the side of the triangle. A network of rhombohedra is thus obtained, and the position of any point can be read off in practically the same manner as in the case of rectangular co-ordinates. Thus the point P in Fig. 75 represents a ternary mixture of the composition A = 0·5, B = 0·2, C = 0·3; the perpendiculars P*a*, P*b*, and P*c* being equal respectively to 0·5, 0·2, and 0·3 of the height of the triangle.

Another method of representation, due to Roozeboom, consists in employing an equilateral triangle, the length of whose *side* is made equal to unity, or one hundred; the sum of the fractional or percentage amounts of the three components being represented therefore by a side of the triangle. In this case the composition of a ternary mixture is obtained by determining, not the *perpendicular* distance of a point P from the three sides of the triangle, but the distance in a direction *parallel* to the sides of the triangle (Fig. 76). Conversely, in order to represent a mixture consisting of *a*, *b*, and *c* parts of the components A, B, and C respectively, one side of the riangle, say AB, is first of all divided into ten or one hundred parts; a portion, Bx = a, is then measured off, and represents the amount of A present. Similarly, a portion, Ax' = b, is measured off and represents the fractional amount of B, while the remainder, xx' = c, represents the amount of C. From x and x' lines are drawn parallel to the sides of the triangle, and the point of intersection, P, represents the composition of the ternary mixture of given composition; for, as is evident from the figure, the distance of the point P from the three sides of the triangle, when measured in directions *parallel* to the sides, is equal to a, b, and c respectively. From the division marks on the side AB, it is seen that the point P in this figure also represents a mixture of 0·5 parts of A, 0·2 parts of B, and 0·3 parts of C.

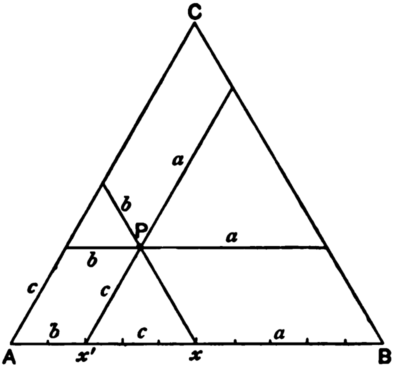

FIG. 76.

In employing the triangular diagram, it will be of use to note a property of the equilateral triangle. A line drawn from one corner of the triangle to the opposite side, represents the composition of all mixtures in which the *relative* amounts of two of the components remain unchanged. Thus, as Fig. 77 shows, if the component C is added to a mixture x, in which A and B are present in the proportions of $a : b$, a mixture x' which is thereby obtained,

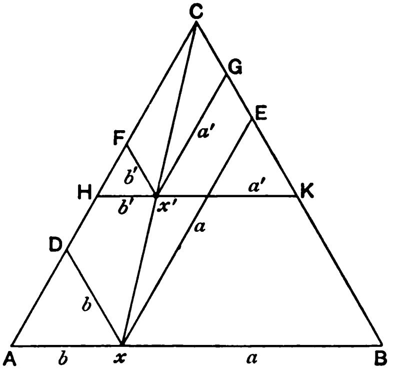

FIG. 77.

lso contains A and B in the ratio $a : b$. For the two triangles ACx and BCx are similar to the two triangles HCx′ and KCx′; and, therefore, Ax : Bx = Hx′ : Kx′. But Ax = Dx and Bx = Ex; further Hx′ = Fx′ and Kx′ = Gx′. Therefore, Dx : Ex = Fx′ : Gx′ = $b : a$. At all points on the line. Cx, therefore, the ratio of A to B is the same.

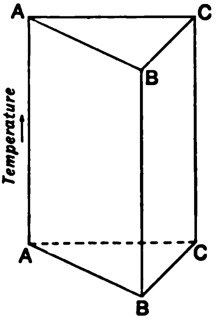

FIG. 78.

If it is desired to represent at the same time the change of another independent variable, *e.g.* temperature, this can be done by measuring the latter along axes drawn perpendicular to the corners of the triangle. In this way a right prism (Fig. 78) is obtained, and each section of his cut parallel to the base represents therefore an *isothermal urface.*

CHAPTER XIV

SOLUTIONS OF LIQUIDS IN LIQUIDS

WE have already seen (p. 93) that when two liquids are brought together, they may mix in all proportions and form one homogeneous liquid phase; or, only partial miscibility may occur, and two phases be formed consisting of two mutually saturated solutions. In the latter case, the concentration of the components in either phase and also the vapour pressure of the system had, at a given temperature, perfectly definite values. In the case of three liquid components, a similar behaviour may be found, although complete miscibility of three components with the formation of only one liquid phase is of much rarer occurrence than in the case of two components. When only partial miscibility occurs, various cases are met with according as the three components form one, two, or three pairs of partially miscible liquids. Further, when two of the components are only partially miscible, the addition of the third may cause either an increase or a diminution in the mutual solubility of these. An increase in the mutual solubility is generally found when the third component dissolves readily in each of the other two; but when the third component dissolves only sparingly in the other two, its addition diminishes the mutual solubility of the latter.

We shall consider here only a few examples illustrating the three chief cases which can occur, viz. (1) A and B, and also B and C are miscible in all proportions, while A and C are only partially miscible. (2) A and B are miscible in all proportions, but A and C and B and C are only partially miscible. (3) A and B, B and C, and A and C are only partially miscible. A, B, and C here represent the three components.

1.—*The three components form only one pair of partially miscible liquids.*

An example of this is found in the three substances: chloro-rm, water, and acetic acid.[1] Chloroform and acetic acid, d water and acetic acid, are miscible with one another in all oportions, but chloroform and water are only partially miscible ith one another. If, therefore, chloroform is shaken with a rger quantity of water than it can dissolve, two layers will be rmed consisting one of a saturated solution of water in hloroform, the other of a saturated solution of chloroform in ater. The composition of these two solutions at a tempera-ure of about 18°, will be represented by the points *a* and *b* in Fig. 79; *a* representing a solution of the composition: chloro-orm, 99 per cent.; water, 1 per cent.; and *b* a solution of the omposition: chloroform, 0·8 per cent.; water, 99·2 per cent. When acetic acid is added, it distributes itself between the two liquid layers, and two conjugate *ternary* solutions, consisting of chloroform, water, and acetic acid are thereby produced which re in equilibrium with one another, and the composition of which ill be represented by two points inside the triangle. In this ay a series of pairs of ternary solutions will be obtained by the addition of acetic acid to the mixture of chloroform and ater. By this addition, also, not only do the two liquid hases become increasingly rich in acetic acid, but the mutual olubility of the chloroform and water increases; so that the yer *a* becomes relatively richer in water, and layer *b* relatively cher in chloroform. This is seen from the following table, hich gives the percentage composition of different conjugate rnary solutions at 18°.

Heavier layer.			Lighter layer.		
hloroform.	Water.	Acetic acid.	Chloroform.	Water.	Acetic acid.
99·01	0·99	0	0·84	99·16	0
91·85	1·38	6·77	1·21	73·69	25·10
80·00	2·28	17·72	7·30	48·58	44·12
70·13	4·12	25·75	15·11	34·71	50·18
67·15	5·20	27·65	18·33	31·11	50·56
59·99	7·93	32·08	25·20	25·39	49·41
55·81	9·58	34·61	28·85	23·28	47·87

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[1] C. R. A. Wright, *Proc. Roy. Soc.*, 1891, **49**. 174; 1892, **50**. 375.

By the continued addition of acetic acid, the composition of the successive conjugate solutions in equilibrium with one another becomes, as the table shows, more nearly the same, and a point is at length reached at which the two solutions become identical. This will therefore be a *critical point* (p. 96). Increased addition of acetic acid beyond this point will lead to a single homogeneous solution.

These relationships are represented graphically by the curve *a*K*b*, Fig. 79. The points on the branch *a*K represent the composition of the solutions relatively rich in chloroform (heavier layer), those on the curve *b*K the composition of solutions relatively rich in water (lighter layer); and the points on these two branches representing conjugate solutions are joined together by "tie-lines." Thus, the points *a'b'* represent conjugate solutions, and the line *a'b'* is a tie-line.

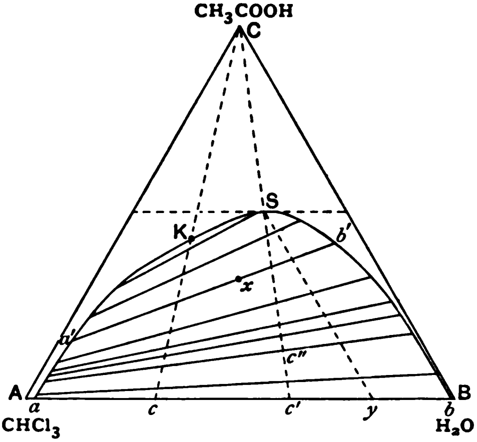

FIG. 79.

Since, now, acetic acid when added to a heterogeneous mixture of chloroform and water does not enter in equal amounts into the two layers, but in amounts depending on its coefficient of distribution between chloroform and water,[1] the tie-lines will not be parallel to AB, but will be inclined at an angle. As the solutions become more nearly the same, the tie-lines diminish in length, and at last, when the conjugate solutions become identical, shrink to a point. For the reason that the tie-lines are, in general, not parallel to the side of the triangle, the critical point at which the tie-line vanishes will not be at the summit of the curve, but somewhere below this, as represented by the point K.

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[1] The distribution coefficient will not remain constant because, apart from other reasons, the mutual solubility of chloroform and water is altered by the addition of the acid.

The curve *a*K*b*, further, forms the boundary between the heterogeneous and homogeneous systems. A mixture of chloroform, water, and acetic acid represented by any point outside the curve *a*K*b*, will form only one homogeneous phase; while any mixture represented by a point within the curve, will separate into two layers having the composition represented by the ends of the tie-line passing through that point. Thus, a mixture of the total composition *x*, will separate into two layers having the composition *a*′ and *b*′ respectively.

Since three components existing in three phases (two liquid and a vapour phase) constitute a bivariant system, the final result, *i.e.* the composition of the two layers and the total vapour pressure, will not depend merely on the temperature, as in the case of two-component systems (p. 100), but also on the composition of the mixture with which we start. At constant temperature, however, all mixtures, the composition of which is represented by a point on one and the same tie-line, will separate into the same two liquid phases, although the relative *amounts* of the two phases will vary. If we omit the vapour phase, the condition of the system will depend on the pressure as well as on the temperature and composition of the initial mixture. By keeping the pressure constant, *e.g.* at atmospheric pressure (by working with open vessels), the system again becomes bivariant. We see, therefore, that the position of the curve *a*K*b*, or, in other words, the composition of the different conjugate ternary solutions, will vary with the temperature, and only with the temperature, if we assume either constancy of pressure or the presence of the vapour phase. Since at the critical point *the condition* is imposed that the two liquid phases *become identical*, one degree of freedom is thereby lost, and therefore only one degree of freedom remains. The critical point, therefore, depends on the temperature, and only on the temperature; always on the assumption, of course, that the pressure is constant, or that a vapour phase is present. Fig. 79, therefore, represents an isothermal (p. 231).

It is of importance to note that the composition of the different ternary solutions obtained by the addition of acetic acid to a heterogeneous mixture of chloroform and water, will depend not only on the amount of acetic acid added, but also on the relative amounts of chloroform and water at the commencement. Suppose, for example, that we start with chloroform and water in the proportions represented by the point *c′* (Fig. 79). On mixing these, two liquid layers having the composition *a* and *b* respectively will be formed. Since by the addition of acetic acid the relative amounts of these two substances in the system as a whole cannot undergo alteration, the total composition of the different ternary systems which will be obtained must be represented by a point on the line C*c′* (p. 230). Thus, for example, by the addition of acetic acid a system may be obtained, the total composition of which is represented by the point *c″*. Such a system, however, will separate into two conjugate ternary solutions, the composition of which will be represented by the ends of the tie-line passing through the point *c″*. So long as the total composition of the system lies below the point S, *i.e.* the point of intersection of the line C*c′* with the boundary curve, two liquid layers will be formed; while all systems having a total composition represented by a point on the line C*c′*, above S, will form only one homogeneous solution.

From the figure, also, it is evident that as the amount of acetic acid is increased, the relative amounts of the two liquid layers formed differ more and more until at S a limiting position is reached, when the amount of the one liquid layer dwindles to nought, and only one solution remains.

The same reasoning can be carried through for different initial amounts of chloroform and water, but it would be fruitless to discuss all the different systems which can be obtained. The reason for the preceding discussion was to show the although the addition of acetic acid to a mixture of chloroform and water will, in all cases, lead ultimately to a limiting system, beyond which homogeneity occurs, that point is not necessarily the critical point. On the contrary, in order that addition of acetic acid shall lead to the critical mixture, it is necessary to start with a binary mixture of chloroform and water in the proportions represented by the point *c*. In this case, addition of acetic acid will give rise to a series of conjugate ternary solutions, the composition of which will gradually approach to one another, and at last become identical.

From the foregoing it will be evident that the amount of acetic acid required to produce a homogenous solution, will depend on the relative amounts of chloroform and water from which we start, and can be ascertained by joining the corner C with the point on the line AB representing the total composition of the initial binary system. The point where this line intersects the boundary curve *a*K*b* will indicate the minimum amount of acetic acid which, under these particular conditions, is necessary to give one homogeneous solution.

Retrograde Solubility.—As a consequence of the fact that acetic acid distributes itself unequally between chloroform and water, and the critical point K, therefore, does not lie at the summit of the curve, it is possible to start with a homogeneous solution in which the percentage amount of acetic acid is greater than at the critical point, and to pass from this first to a heterogenous and then again to a homogenous system merely by altering the relative amounts of chloroform and water. This phenomenon, to which the term *retrograde solubility* is applied, will be observed not only in the case of chloroform, water, and acetic acid, but in all other systems in which the critical point lies below the highest point of the boundary curve for heterogeneous systems. This will be seen from the diagram, Fig. 80. Starting with the homogeneous system represented by x, in which, therefore, the concentration of C is greater than in the critical mixture (K), if the relative amounts of A and B are altered in the direction xx', while the amount of C is maintained constant, the system will become heterogeneous when the composition reaches the point y, and will remain heterogeneous with changing composition until the point *y'* is passed, when it will again become homogeneous. If the relative concentration of C is increased above that represented by the line SS, this phenomenon will, of course, no longer be observed.

Relationships similar to those described for chloroform, water, and acetic acid are also found in the case of a number of other trios, *e.g.* ether, water, and alcohol; chloroform, water, and alcohol.[1] They have also been observed in the case of a considerable number of molten metals.[2] Thus, molten lead and silver, as well as molten zinc and silver, mix in all proportions; but molten lead and zinc are only partially miscible with one another. When melted together, therefore, the last two metals will separate into two liquid layers, one rich in lead, the other rich in zinc. If silver is now added, and the temperature maintained above the freezing point of the mixture, the silver passes for the most part, in accordance with the law of distribution, into the upper layer, which is rich in zinc; silver being more soluble in molten zinc than in molten lead. This is clearly shown by the following figures:—[3]

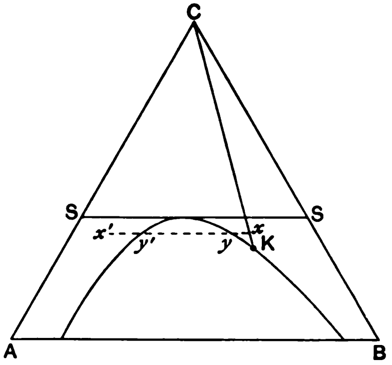

FIG. 80.

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[1] Bancroft, *Physical Review*, 1895, **3**. 21; Schreinemakers, *Zeitschr. physikal. Chem.*, 1897, **23**. 652, and subsequent volumes.

[2] C. R. A. Wright, *Proc. Roy. Soc.*, 1889–1893.

[3] C. R. A. Wright, *Proc. Roy. Soc.*, 1892, **50**. 390.

Heavier alloy.			Lighter alloy.		
Percentage amount of			Percentage amount of		
Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.
1·25	96·69	2·06	38·91	3·12	57·97
1·71	96·43	1·86	45·01	3·37	51·62
5·55	93·16	1·29	54·93	4·21	40·86

The numbers in the same horizontal row give the composition of the conjugate alloys, and it is evident that the upper layer consists almost entirely of silver and zinc. On allowing the mixture to cool slightly, the upper layer solidifies first, and can be separated from the still molten lead layer. It is on this behaviour of silver towards a mixture of molten lead and zinc that the Parkes's method for the desilverization of lead depends.[1] If aluminium is also added, a still larger proportion of silver passes into the lighter layer, and the desilverization of the lead is more complete.[2]

The Influence of Temperature.—As has already been said, a ternary system existing in three phases possesses two degrees of freedom; and the state of the system is therefore dependent not only on the relative concentration of the components, but also on the temperature. As the temperature changes, therefore, the boundary curve of the heterogeneous system will also alter; and in order to represent this alteration we shall make use of the right prism, in which the temperature is measured upwards. In this way the boundary curve passes into a boundary surface (called a dineric surface), as shown in Fig. 81. In this figure the curve *akb* is the isothermal for the ternary system; the curve *a*K*b* shows the change in the *binary* system AB with the temperature, with

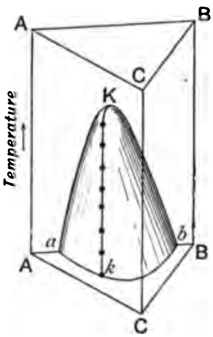

FIG. 81.

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[1] Bodländer, *Berg- und Hüttenmänn. Ztg.*, 1897, 56. 331.

[2] C. R. A. Wright, *Proc. Roy. Soc.*, *loc. cit.*

a critical point at K. This curve has the same meaning as those given in Chapter VI. The curve *k*K is a critical curve joining together the critical points of the different isothermals. In such a case as is shown in Fig. 81, there does not exist any real critical temperature for the ternary system, for as the temperature is raised, the amount of C in the "critical" solution becomes less and less, and at K only two components, A and B, are present. In the case, however, represented in Fig. 82, a real ternary critical point is found. In this figure *ak'b* is an isothermal, *ak''* is the curve for the binary system, and K is the ternary critical point. All points outside the helmet-shaped boundary surface represent homogeneous ternary solutions, while all points within the surface belong to heterogeneous systems. Above the temperature of the point K, the three components are miscible in all proportions. An example of a ternary system yielding such a boundary surface is that consisting of phenol, water, and acetone.[1]

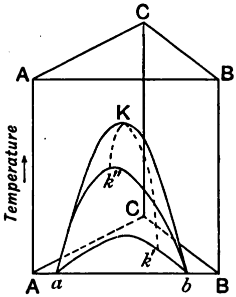

FIG. 82.

In this case the critical temperature K is 92°, and the composition at this ternary critical point is—

Water	59	per cent.
Acetone	12	„
Phenol	29	„

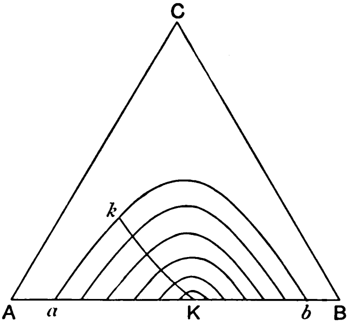

FIG. 83.

The difference between the two classes of systems just mentioned, is seen very clearly by a glance at the Figs. 83 and 84, which show the projection of the isothermals on the base of the prism. In Fig. 83, the projections yield paraboloid curves, the two branches of which are cut by one side of the triangle; and the critical point is represented by a point on

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[1] Schreinemakers, *Zeitschr. physikal. Chem.*, 1900, **33.** 78.

is side. In the second case (Fig. 84), however, the pro-
ctions of the isothermals form ellipsoidal curves surrounding
e supreme critical point,
hich now lies *inside the*
iangle. At lower tempera-
res, these isothermal boun-
ary curves are cut by a side
f the triangle; at the critical
mperature, k'', of the binary
stem AB, the boundary
rve *touches* the side AB,
hile at still higher tempera-
res the boundary curve
omes to lie entirely within
e triangle. At any given
mperature, therefore, between the critical point of the binary
stem (k''), and the supreme critical point of the ternary system
K), each pair of the three components are miscible with one
nother in all proportions; for the region of heterogeneous
stems is now bounded by a closed curve lying entirely within
e triangle. Outside this curve only homogeneous systems
re found. Binary mixtures, therefore, represented by any
oint on one of the sides of the triangle must be homogeneous,
r they all lie outside the boundary curve for heterogeneous
tates.

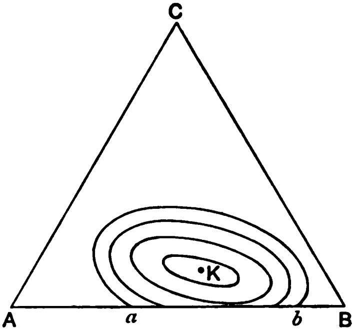

FIG. 84.

2. *The three components can form two pairs of partially*
iscible liquids.

In the case of the three components water, alcohol, and
uccinic nitrile, water and alcohol are miscible in all propor-
ons, but not so water and succinic nitrile, or alcohol and
uccinic nitrile.

As we have already seen (p. 120), water and succinic
itrile can form two liquid layers between the temperatures
8·5° and 55·5°; while alcohol and nitrile can form two liquid
ayers betwen 13° and 31°. If, then, between these two
emperature limits, alcohol is added to a heterogeneous mixture
f water and nitrile, or water is added to a mixture of alcohol
nd nitrile, two heterogeneous ternary systems will be formed,

and two boundary curves will be obtained in the triangular diagram, as shown in Fig. 85.[1] On changing the temperature, the boundary curves will also undergo alteration, in a manner similar to that just discussed. As the temperature falls, the two curves will spread out more and more into the centre of

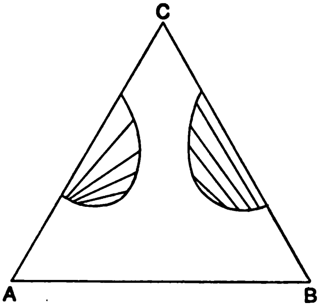

FIG. 85.

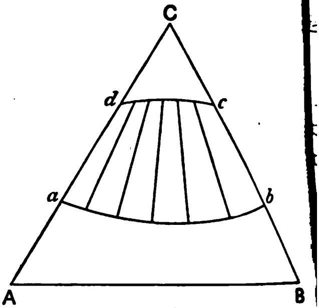

FIG. 86.

the triangle, and might at last meet one another; while at still lower temperatures we may imagine the curves still further expanding so that the two heterogeneous regions flow into one another and form a *band* on the triangular diagram (Fig. 86). This, certainly, has not been realized in the case of the three components mentioned, because at a temperature higher than that at which the two heterogeneous regions could fuse together, solid separates out.

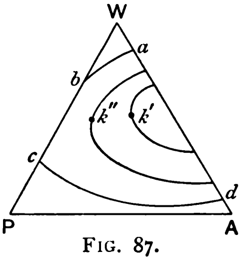

FIG. 87.

The gradual expansion of a paraboloid into a band-like area of heterogeneous ternary systems, has, however, been observed in the case of water, phenol, and aniline.[2] In Fig. 87 are shown three isothermals, viz. those for 148°, 95°, and 50°. At 148°, water and aniline form two layers having the composition—

Water, 83·5 per cent. } and { water, 20 per cent.
Aniline, 16·5 ,, } and { aniline, 80 ,,

---

[1] Schreinemakers, *Zeitschr. physikal. Chem.*, 1898, **27**. 95.

[2] Schreinemakers, *Zeitschr. physikal. Chem.*, 1899, **29**. 577.

ıe critical point *k*′ has the composition—

Water, 65; phenol, 13·2; aniline, 21·8 per cent.

95°, the composition of the two binary solutions is—

Water, 93 per cent. } and { water, 8 per cent.
Aniline, 7 ,, } { aniline, 92 ,,

the point *k*″ has the composition

Water, 69·9; phenol, 26·6; aniline, 3·5 per cent.

50°, the region of heterogeneous states now forms a and the two layers formed by water and aniline have the ɔsition—

Water, 96·5 per cent. } and { water, 5·5 per cent.
Aniline, 3·5 ,, } { aniline, 94·5 ,,

the two layers formed by water and phenol have the ɔsition—

Water, 89 per cent. } and { water, 38 per cent.
Phenol, 11 ,, } { phenol, 62 ,,

ixtures of water, phenol, and aniline, therefore, the com- ɔn of which is represented by any point within the band vill form two ternary solutions; while if the composition :esented by a point outside the band, only one homo- ıs solution will be produced.

The three components form three pairs of partially le liquids.

ıe third chief case can occur is that no the components are etely miscible with ıother. In this case, ɔre, we shall obtain paraboloid boundary ;, as shown in Fig. [f, now, we imagine three curves to ex- ın towards the centre : triangle, as might a, for example, by lowering the temperature, a point will

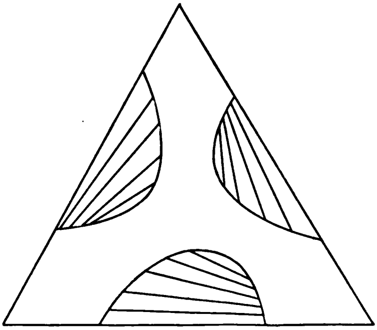

FIG. 88.

be reached at which the curves partly overlap, and we shall get the appearance shown in Fig. 89.

The points *a*, *b*, and *c* represent the points where the three curves cut, and the triangle *abc* is a region where the curves overlap. From this diagram we can see that any mixture having a composition represented by a point in one of the clear spaces at the corners of the larger triangle, will form a homogeneous solution; if the composition corresponds to any point lying in one of the quadrilateral regions x_1, x_2 or x_3, two ternary solutions will be formed; while, if the composition is represented by any point in the inner triangle, separation into three layers will occur.

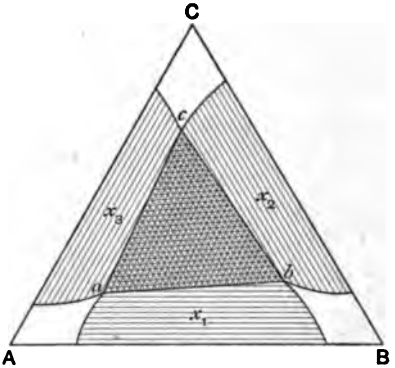

FIG. 89.

Since in the clear regions at the corners of the triangle we have three components in two phases, liquid and vapour, the systems have three degrees of freedom. At constant temperature, therefore, the condition of the system is not defined until the concentrations of two of the components are fixed. A system belonging to one of the quadrilateral spaces has, as we have seen, two degrees of freedom; besides the temperature, one concentration must be fixed. Lastly, a system the composition of which falls within the inner triangle *abc*, will form three layers, and will therefore possess only one degree of freedom. If the temperature is fixed, the composition of the three layers is also determined, viz. that of the points *a*, *b*, and *c* respectively; and a change in the composition of the original mixture can lead only to a difference in the relative amounts of the three layers, not to a difference in their composition.

An example of a system which can form three liquid phases *is found* in water, ether, and succinic nitrile.[1]

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[1] Schreinemakers, *Zeitschr. physikal. Chem.*, 1898, 25. 543.

CHAPTER XV

PRESENCE OF SOLID PHASES

A. The Ternary Eutectic Point.—In passing to the con- eration of those ternary systems in which one or more solid ases can exist together with one liquid phase, we shall first cuss not the solubility curves, as in the case of two-com- nent systems, but the simpler relationships met with at the ezing point. That is, we shall first of all examine the ezing point curves of ternary systems.

Since it is necessary to take into account not only the nging composition of the liquid phase, but also the variation the temperature, we shall employ right prism for the graphic re- sentation of the systems, as wn in Fig. 90. A, B, and C in figure, therefore, denote the lting points of the pure com- nents. If we start with the com- nent A at its melting point, and B, which is capable of dissolving liquid A, the freezing point of A l be lowered; and, similarly, the ezing point of B by addition of A. this way we get the freezing point rve Ak_1B for the binary system; being an eutectic point. This curve will of course lie in the ne formed by one face of the prism. In a similar manner we tain the freezing point curves Ak_2C and Bk_3C. These curves e the composition of the binary liquid phases in equilibrium

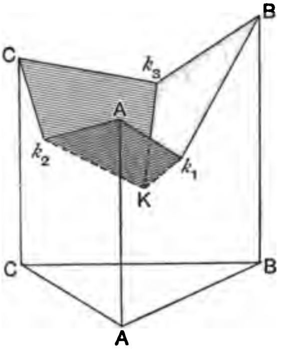

FIG. 90.

with one of the pure components, or at the eutectic points, with a mixture of two solid components. If, now, to the system represented say by the point k_1, a small quantity of the third component, C, is added, the temperature at which the two solid phases A and B can exist in equilibrium with the liquid phase is lowered; and this depression of the eutectic point is all the greater the larger the addition of C. In this way we obtain the curve k_1K, which slopes inwards and downwards, and indicates the varying composition of the ternary liquid phase with which a mixture of solid A and B are in equilibrium. Similarly, the curves k_2K and k_3K are the corresponding eutectic curves for A and C, and B and C in equilibrium with ternary solutions. At the point K, the three solid components are in equilibrium with the liquid phase; and this point, therefore, represents *the lowest temperature attainable with the three components given.* Each of the ternary eutectic curves, as they may be called, is produced by the intersection of two surfaces, while at the ternary eutectic point, three surfaces, viz. Ak_1Kk_2, Bk_1Kk_3 and Ck_1Kk_3 intersect. Any point on one of these surfaces represents a ternary solution in equilibrium with only one component in the solid state; the lines or curves of intersection of these represent equilibria with two solid phases, while at the point K, the ternary eutectic point, there are three solid phases in equilibrium with a liquid and a vapour phase. The surfaces just mentioned represent bivariant systems. One component in the solid state can exist in equilibrium with a ternary liquid phase under varying conditions of temperature and concentration of the components in the solution; and before the state of the system is defined, these two variables, temperature and composition of the liquid phase, must be fixed. On the other hand, the curves formed by the intersection of these planes represent univariant systems; at a given temperature two solid phases can exist in equilibrium with a ternary solution, only when the latter has a definite composition. Lastly, the ternary eutectic point, K, represents an invariant system; three solid phases can exist in equilibrium with a ternary solution, only when the latter has one fixed composition and when the temperature has a definite value. This eutectic point, therefore, has a perfectly definite position, depending only on the nature of the three components.

Instead of employing the prism, the change in the composition of the ternary solutions can also be indicated by means of the *projections* of the curves k_1K, k_2K, and k_3K on the base of the prism, the particular temperature being written beside the different eutectic points and curves. This is shown in Fig. 91.

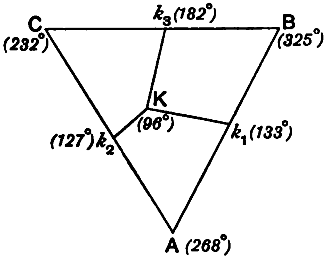

FIG. 91.

The numbers which are given in this diagram refer to the eutectic points for the system bismuth—lead—tin, the data for which are as follows :—[1]

Melting point of pure metal.	Percentage composition of binary eutectic mixture.			Temperature of binary eutectic point.
	Bi	Pb	Sn	
Bismuth, 268°	55	45	—	Bi—Pb, 127°
Lead, 325°	58	—	42	Bi—Sn, 133°
Tin, 232°	—	37	63	Pb—Sn, 182°

Percentage composition of ternary eutectic mixture.			Temperature of ternary eutectic point.
Bi	Pb	Sn	
52	32	16	96°

Formation of Compounds.—In the case just discussed, the components crystallized out from solution in the pure state. If, however, combination can take place between two of the components, the relationships will be somewhat different; the curves which are obtained in such a case being represented in Fig. 92. From the figure, we see that the two components B

and C form a compound, and the freezing point curve of the binary system has therefore the form shown in Fig. 64 (p. 207). Further, there are two *ternary* eutectic points, K_1 and K_2, the solid phases present being A, B, and compound, and A, C, and compound respectively.

---

[1] Charpy, *Compt. rend.*, 1898, **126**. 1569. Compare the curves for the system KNO_3—$NaNO_3$—$LiNO_3$ (H. R. Carveth, Journ. Physical *Chem.*, *1898*, **2**. *209*). Also alloys of Pb—Sn—Bi (E. S. Shepherd, *Journ. Physical Chem.*, 1902, **6**. 527).

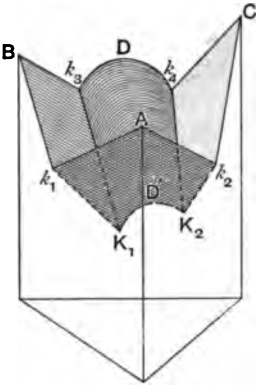

FIG. 92.

The particular point, now, to which it is desired to draw attention is this. Suppose the ternary eutectic curves projected on a plane parallel to the face of the prism containing B and C, *i.e.* suppose the concentrations of the two components B and C, between which interaction can occur, expressed in terms of a constant amount of the third component A,[1] curves will then be obtained which are in every respect analogous to the freezing point curves of binary systems. Thus, suppose the eutectic curves k_1K and k_2K in Fig. 90 projected on the face BC of the prism, then evidently a curve will be obtained consisting of two branches meeting in an eutectic point. On the other hand, the projection of the ternary eutectic curves in Fig. 92 on the face BC of the prism, will give a curve consisting of three portions, as shown by the outline $k_1K_1K_2k_2$ in Fig. 92.

Various examples of this have been studied, and the following table contains some of the data for the system ethylene bromide (A), picric acid (B), and β-naphthol (C), obtained by Bruni.[2]

---

[1] It should be remembered that in the triangular diagram a *line* parallel to one of the sides indicates, at a given temperature, a constant amount of the component represented by the opposite corner of the triangle; and, hence, points in a *plane*, parallel to one face of a right prism, will indicate for different temperatures, variation in the amounts of two components, but constancy in the amount of the third.

[2] *Gazzetta chim. ital.*, 1898, **28**. II. 520.

	Temperature.	Solid phases present.
oint k_1	9·41°	Ethylene bromide, picric acid.
urve k_1K_1 . . .	—	,, ,,
oint K_1	9·32°	Ethylene bromide, picric acid, and β-naphthol picrate.
urve $K_1D'K_2$ . .	—	Ethylene bromide, β-napthol picrate.
int D'	9·75°	,, ,, ,, ,,
int K_2	8·89°	,, ,, β-naphthol, and picrate.
rve K_2k_2 . . .	—	,, ,, β-napthol.
int k_2	9·04°	,, ,, ,,

From what has been said, it will be apparent that if the nary eutectic curve of a three-component system (in which e of the components is present in constant amount) is deter-ned, it will be possible to state, from the form of curve tained, whether or not the two components present in varying iount crystallize out pure or combine with one another to m a compound. It may be left to the reader to work out curves for the other possible systems; but it will be apparent, it the projections of the ternary eutectic curves in the manner ren will yield a series of curves alike in all points to the iary curves given in Figs. 63–65, pp. 206–208.

Since, from the method of investigation, the temperatures the eutectic curves will depend on the melting point of the ird component (A), it is possible, by employing substances th widely differing melting points, to investigate the inter-tion of the two components (*e.g.* two optical antipodes) B d C over a range of temperature; and thus determine the ıge of stability of the compound, if one is formed. Since, some cases, two substances which at one temperature form ixed crystals combine at another temperature to form definite compound, the relationships which have just been scribed can be employed, and indeed, have been employed, determine the temperature at which this change occurs.[1] y means of this method, Adriani found that below 103° *i*-mphoroxime exists as a racemic compound, while above that temperature it occurs as a racemic mixed crystal[1] (*cf.* p. 217).

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[1] Bruni, *Gazzetta chim. ital.*, 1898, **28**. II. 508; 1900, **30**. I. 35.

B. Equilibria at Higher Temperatures. Formation of Double Salts.—After having studied the relationships which are found in the neighbourhood of the freezing points of the components, we now pass to the discussion of the equilibria which are met with at higher temperatures. In this connection we shall confine the discussion entirely to the systems formed of two salts and water, dealing more particularly with those cases in which the water is present in relatively large amount and acts as solvent. Further, in studying these systems, one restriction must be made, viz. that the single salts are salts either of the same base or of the same acid; or are, in other words, capable of yielding a common ion in solution. Such a restriction is necessary, because otherwise the system would be one not of three but of four components.[2]

Transition Point.—As is very well known, there exist a number of hydrated salts which, on being heated, undergo apparent partial fusion; and in Chapter V. the behaviour of such hydrates was more fully studied in the light of the Phase Rule. Glauber's salt, or sodium sulphate decahydrate, for example, on being heated to a temperature of about 32·5°, partially liquefies, owing to the fact that the water of crystallization is split off and anhydrous sodium sulphate formed, as shown by the equation—

$$Na_2SO_4,10H_2O = Na_2SO_4 + 10H_2O$$

The temperature of 32·5°, it was learned, constituted a *transition point* for the decahydrate and anhydrous salt plus water; decomposition of the hydrated salt occurring above this temperature, combination of the anhydrous salt and water below it.

Analogous phenomena are met with in systems constituted of two salts and water in which the formation of double salts can take place. Thus, for example, if *d*-sodium potassium tartrate is heated to above 55°, apparent partial fusion occurs, and the two single salts, *d*-sodium tartrate and *d*-potassium tartrate, are deposited, the change which occurs being represented by the equation—

---

[1] *Zeitschr. physikal. Chem.*, 1900, **36**. 168.

[2] For a discussion of these systems, see van't Hoff, *Bildung und Spaltung von Doppelsalzen* (Leipzig, 1897).

$$4NaKC_4O_6H_4,4H_2O = 2Na_2C_4O_6H_4,2H_2O + 2K_2C_4O_6H_4\tfrac{1}{2}H_2O + 11\,H_2O$$

On the other hand, if sodium and potassium tartrates are mixed with water in the proportions shown on the right side of the equation, the system will remain partially liquid so long as the temperature is maintained above 55° (in a closed vessel to prevent loss of water), but on allowing the temperature to fall below this point, complete solidification will ensue, owing to the formation of the hydrated double salt. Below 55°, therefore, the hydrated double salt is the stable system, while above this temperature the two single salts plus saturated solution are stable.[1]

A similar behaviour is found in the case of the double salt copper dipotassium chloride ($CuCl_2,2KCl,2H_2O$ or $CuK_2Cl_4,2H_2O$).[2] When this salt is heated to 92°, partial liquefaction occurs, and the original blue plate-shaped crystals give place to brown crystalline needles and white cubes; while on allowing the temperature to fall, re-formation of the blue double salt ensues. The temperature 92° is, therefore, a transition point at which the reversible reaction—

$$CuK_2Cl_4,2H_2O \rightleftarrows CuKCl_3 + KCl + 2H_2O$$

takes place.

The decomposition of sodium potassium tartrate, or of copper dipotassium chloride, differs in so far from that of Glauber's salt that *two* new solid phases are formed; and in the case of copper dipotassium chloride, one of the decomposition products is itself a double salt.

In the two examples of double salt decomposition which have just been mentioned, sufficient water was yielded to cause a partial liquefaction; but other cases are known where this is not so. Thus, when copper calcium acetate is heated to a temperature of 75°, although decomposition of the double salt into the two single salts occurs as represented by the equation[1]—

---

[1] Van Leeuwen, *Zeitschr. physikal. Chem.*, 1897, **23**. 35.

[2] Meyerhoffer, *Zeitschr. physikal. Chem.*, 1889, **3**. 336; 1890, **5**. 97.

$$CuCa(C_2H_3O_2)_4,8H_2O = Cu(C_2H_3O_2)_2,H_2O + Ca(C_2H_3O_2)_2,H_2O + 6H_2O$$

the amount of water split off is insufficient to give the appearance of partial fusion, and, therefore, only a change in the crystals is observed.

The preceding examples, in which decomposition of the double salt was effected by a rise of temperature, were chosen for first consideration as being more analogous to the case of Glauber's salt; but not a few examples are known where the reverse change takes place, formation of the double salt occurring *above* the transition point, and decomposition into the constituent salts below it. Instances of this behaviour are found in the case of the formation of astracanite from sodium and magnesium sulphates, and of sodium ammonium racemate from the two sodium ammonium tartrates, to which reference will be made later. Between these various systems, however, there is no essential difference; and whether decomposition or formation of the double salt occurs at temperatures above the transition point, will of course depend on the heat of change at that point. For, in accordance with van't Hoft's law of movable equilibrium (p. 56), that change will take place at the higher temperature which is accompanied by an absorption of heat. If, therefore, the formation of the double salt from the single salts is accompanied by an absorption of heat, the double salt will be formed from the single salts on raising the temperature; but if the reverse is the case, then the double salt on being heated will decompose into the constituent salts.[2]

In those cases, now, which have so far been studied, th change at the transition point is accompanied by a taking u or a splitting off of water; and *in such cases the general rule ca be given, that if the water of crystallization of the two constituen*

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[1] Reicher, *Zeitschr. physikal. Chem.*, 1887, **1.** 220.

[2] For other examples of the formation and decomposition of doubl *salts* at a transition point, the reader is referred to the work by van't Hof already cited, on the *Bildung und Spaltung von Doppelsalzen*; or to Ba croft, *Phase Rule*, p. 180.

salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature (*e.g.* astracanite from sodium and magnesium sulphates); *but if the double salt contains more water of crystallization than the two single salts, increase of temperature will effect the decomposition of the double salt.* When we seek for the connection between this rule and the law of van't Hoff, it is found in the fact that the heat effect involved in the hydration or dehydration of the salts is much greater than that of the other changes which occur, and determines, therefore, the sign of the total heat effect.[1]

Vapour Pressure. Quintuple Point.—In the case of Glauber's salt, we saw that at a certain temperature the vapour pressure curve of the hydrated salt cut that of the saturated solution of anhydrous sodium sulphate. That point, it will be remembered, was a quadruple point at which the four phases sodium sulphate decahydrate, anhydrous sodium sulphate, solution, and vapour, could co-exist; and was also the point of intersection of the curves for four univariant systems. In the case of the formation of double salts, similar relationships are met with; and also certain differences, due to the fact that we are now dealing with systems of three components. Two cases will be chosen here for brief description, one in which formation, the other in which decomposition of the double salt occurs with rise of temperature.

On heating a mixture of sodium sulphate decahydrate and magnesium sulphate heptahydrate, it is found that at 22° partial liquefaction occurs with formation of astracanite. At this temperature, therefore, there can coexist the five phases—

$$Na_2SO_4,10H_2O;\ MgSO_4,7H_2O;\ Na_2Mg(SO_4)_2,4H_2O;$$
$$\text{solution; vapour.}$$

This constitutes, therefore, a *quintuple point*; and since there are three components present in five phases, the system is invariant. This point, also, will be the point of intersection of curves for five univariant systems, which, in this case, must each be composed of four phases. These systems are—

---

[1] Bancroft, *Phase Rule*, p. 183.

I. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; vapour.

II. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; solution; vapour.

III. $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

IV. $Na_2SO_4,10H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

V. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution.

On representing the vapour pressures of these different systems graphically, a diagram is obtained such as is shown in Fig. 93,[1] the curves being numbered in accordance with the above list. When the system I. is heated, the vapour pressure increases until at the quintuple point the liquid phase (solution) is formed, and it will then depend on the relative amounts of the different phases whether on further heating there is formed system III., IV., or V. If either of the first two is produced, we shall obtain the vapour pressure of the solutions saturated with respect to both double salt and one of the single salts; while if the vapour phase disappears, there will be obtained the pressure of the condensed systems formed of double salt, two single salts and solution. This curve, therefore, indicates the *change of the transition point with pressure;* and since in the ordinary determinations of the transition point in open vessels, we are in reality dealing with condensed systems under the pressure of 1 atm., it will be evident that the transition point does not accurately coincide with the quintuple point (at which the system is under the pressure of its own vapour). As in the case of other condensed systems, however, pressure has only a slight influence on the temperature of the transition point. Whether or not pressure raises or lowers the transition point will depend on whether transformation is accompanied by an increase or

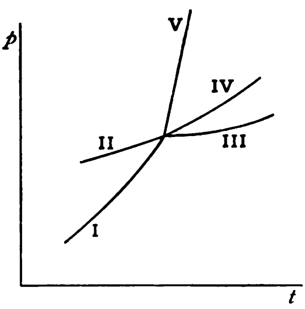

FIG. 93.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1888, **2**. 514.

diminution of volume (theorem of Le Chatelier, p. 56). In the case of the formation of astracanite, expansion occurs, and the transition point will therefore be raised by increase of pressure. Although measurements have not been made in the case of this system, the existence of such a curve has been experimentally verified in the case of copper and calcium acetates and water (v. *infra*).

The vapour pressure diagram in the case of copper calcium acetate and water (Fig. 94), is almost the reverse of that already discussed. In this case, the double salt decomposes on heating, and the decomposition is accompanied by a contraction. Curve I. is the vapour pressure curve for double salt, two single salts (p. 252), and vapour; curves II. and III. give the vapour pressures of solutions saturated with respect to double salt and one of the single salts; curve IV. is the curve of pressures for the solutions saturated with respect to the two single salts; while curve V. again represents the change of the transition point with pressure. On examining this diagram, it is seen that whereas astracanite could exist both above and below the quintuple point, copper calcium acetate can exist only *below* the quintuple point. This behaviour is found only in those cases in which the double salt is decomposed by rise of temperature, and where the decomposition is accompanied by a diminution of volume.[1]

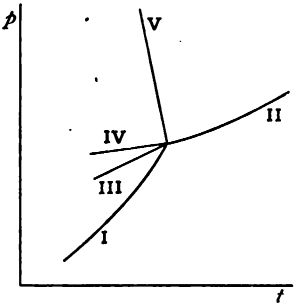

FIG. 94.

As already mentioned, the decomposition of copper calcium acetate into the single salts and saturated solution is accompanied by a contraction, and it was therefore to be expected that increase of pressure would *lower* the transition point. This expectation of theory was confirmed by experiment, for van't Hoff and Spring found that although the transition point under atmospheric pressure is about 75°, decomposition of the with one of the pure components, or at the eutectic points, with a mixture of two solid components. If, now, to the system represented say by the point k_1, a small quantity of the third component, C, is added, the temperature at which the two solid phases A and B can exist in equilibrium with the liquid phase is lowered; and this depression of the eutectic point is all the greater the larger the addition of C. In this way we obtain the curve k_1K, which slopes inwards and downwards, and indicates the varying composition of the ternary liquid phase with which a mixture of solid A and B are in equilibrium. Similarly, the curves k_2K and k_3K are the corresponding eutectic curves for A and C, and B and C in equilibrium with ternary solutions. At the point K, the three solid components are in equilibrium with the liquid phase; and this point, therefore, represents *the lowest temperature attainable with the three components given.* Each of the ternary eutectic curves, as they may be called, is produced by the intersection of two surfaces, while at the ternary eutectic point, three surfaces, viz. Ak_1Kk_2, Bk_1Kk_3 and Ck_1Kk_3 intersect. Any point on one of these surfaces represents a ternary solution in equilibrium with only one component in the solid state; the lines or curves of intersection of these represent equilibria with two solid phases, while at the point K, the ternary eutectic point, there are three solid phases in equilibrium with a liquid and a vapour phase. The surfaces just mentioned represent bivariant systems. One component in the solid state can exist in equilibrium with a ternary liquid phase under varying conditions of temperature and concentration of the components in the solution; and before the state of the system is defined, these two variables, temperature and composition of the liquid phase, must be fixed. On the other hand, the curves formed by the intersection of these planes represent univariant systems; at a given temperature two solid phases can exist in equilibrium with a ternary solution, only when the latter has a definite composition. Lastly, the ternary eutectic point, K, represents an invariant system; three solid phases can exist in equilibrium with a ternary solution, only when the latter has one fixed composition and when the temperature has a definite value. This eutectic point, therefore, has a perfectly definite position, depending only on the nature of the three components.

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[1] *Roozeboom, Zeitschr. physikal. Chem.*, 1887, 1. 227.

Instead of employing the prism, the change in the composition of the ternary solutions can also be indicated by means of the *projections* of the curves k_1K, k_2K, and k_3K on the base of the prism, the particular temperature being written beside the different eutectic points and curves. This is shown in Fig. 91.

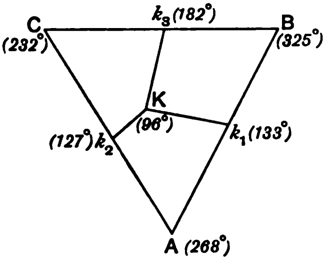

FIG. 91.

The numbers which are given in this diagram refer to the eutectic points for the system bismuth—lead—tin, the data for which are as follows :—[1]

Melting point of pure metal.	Percentage composition of binary eutectic mixture.			Temperature of binary eutectic point.
	Bi	Pb	Sn	
Bismuth, 268°	55	45	—	Bi—Pb, 127°
Lead, 325°	58	—	42	Bi—Sn, 133°
Tin, 232°	—	37	63	Pb—Sn, 182°

Percentage composition of ternary eutectic mixture.			Temperature of ternary eutectic point.
Bi	Pb	Sn	
52	32	16	96°

Formation of Compounds.—In the case just discussed, the components crystallized out from solution in the pure state. If, however, combination can take place between two of the components, the relationships will be somewhat different; the curves which are obtained in such a case being represented in Fig. 92. From the figure, we see that the two components B

and C form a compound, and the freezing point curve of the binary system has therefore the form shown in Fig. 64 (p. 207). Further, there are two *ternary* eutectic points, K_1 and K_2, the solid phases present being A, B, and compound, and A, C, and compound respectively.

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[1] Charpy, *Compt. rend.*, 1898, **126**. 1569. Compare the curves for the system KNO_3—$NaNO_3$—$LiNO_3$ (H. R. Carveth, *Journ. Physical Chem.*, 1898, **2**. 209). Also alloys of Pb—Sn—Bi (E. S. Shepherd, *Journ. Physical Chem.*, 1902, **6**. 527).

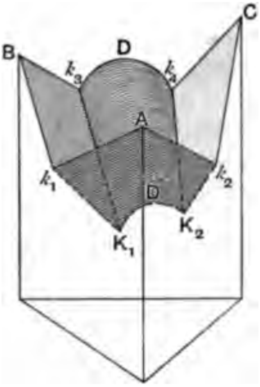

FIG. 92.

The particular point, now, to which it is desired to draw attention is this. Suppose the ternary eutectic curves projected on a plane parallel to the face of the prism containing B and C, *i.e.* suppose the concentrations of the two components B and C, between which interaction can occur, expressed in terms of a constant amount of the third component A,[1] curves will then be obtained which are in every respect analogous to the freezing point curves of binary systems. Thus, suppose the eutectic curves k_1K and k_2K in Fig. 90 projected on the face BC of the prism, then evidently a curve will be obtained consisting of two branches meeting in an eutectic point. On the other hand, the projection of the ternary eutectic curves in Fig. 92 on the face BC of the prism, will give a curve consisting of three portions, as shown by the outline $k_1K_1K_2k_2$ in Fig. 92.

Various examples of this have been studied, and the following table contains some of the data for the system ethylene bromide (A), picric acid (B), and β-naphthol (C), obtained by Bruni.[2]

---

[1] It should be remembered that in the triangular diagram a *line* parallel to one of the sides indicates, at a given temperature, a constant amount of the component represented by the opposite corner of the triangle; and, hence, points in a *plane*, parallel to one face of a right prism, will indicate for different temperatures, variation in the amounts of two components, but constancy in the amount of the third.

[2] *Gazzetta chim. ital.*, 1898, **28**. II. 520.

	Temperature.	Solid phases present.
Point k_1	9·41°	Ethylene bromide, picric acid.
Curve k_1K_1	—	,, ,,
Point K_1	9·32°	Ethylene bromide, picric acid, and β-naphthol picrate.
Curve $K_1D'K_2$	—	Ethylene bromide, β-napthol picrate.
Point D'	9·75°	,, ,, ,, ,,
Point K_2	8·89°	,, ,, β-naphthol, and picrate.
Curve K_2k_2	—	,, ,, β-napthol.
Point k_2	9·04°	,, ,, ,,

From what has been said, it will be apparent that if the ternary eutectic curve of a three-component system (in which one of the components is present in constant amount) is determined, it will be possible to state, from the form of curve obtained, whether or not the two components present in varying amount crystallize out pure or combine with one another to form a compound. It may be left to the reader to work out the curves for the other possible systems; but it will be apparent, that the projections of the ternary eutectic curves in the manner given will yield a series of curves alike in all points to the binary curves given in Figs. 63–65, pp. 206–208.

Since, from the method of investigation, the temperatures of the eutectic curves will depend on the melting point of the third component (A), it is possible, by employing substances with widely differing melting points, to investigate the interaction of the two components (*e.g.* two optical antipodes) B and C over a range of temperature; and thus determine the range of stability of the compound, if one is formed. Since, in some cases, two substances which at one temperature form mixed crystals combine at another temperature to form a definite compound, the relationships which have just been described can be employed, and indeed, have been employed, to determine the temperature at which this change occurs.[1] By means of this method, Adriani found that below 103° *i-camphoroxime exists* as a racemic compound, while above that temperature it occurs as a racemic mixed crystal[1] (c p. 217).

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[1] *Bruni, Gazzetta chim. ital.*, 1898, **28**. II. 508; 1900, **30**. I. 35.

B. Equilibria at Higher Temperatures. Formation of Double Salts.—After having studied the relationships which are found in the neighbourhood of the freezing points of the components, we now pass to the discussion of the equilibria which are met with at higher temperatures. In this connection we shall confine the discussion entirely to the systems formed of two salts and water, dealing more particularly with those cases in which the water is present in relatively large amount and acts as solvent. Further, in studying these systems, one restriction must be made, viz. that the single salts are salts either of the same base or of the same acid; or are, in other words, capable of yielding a common ion in solution. Such a restriction is necessary, because otherwise the system would be one not of three but of four components.[2]

Transition Point.—As is very well known, there exist a number of hydrated salts which, on being heated, undergo apparent partial fusion; and in Chapter V. the behaviour of such hydrates was more fully studied in the light of the Phase Rule. Glauber's salt, or sodium sulphate decahydrate, for example, on being heated to a temperature of about 32·5°, partially liquefies, owing to the fact that the water of crystallization is split off and anhydrous sodium sulphate formed, as shown by the equation—

$$Na_2SO_4,10H_2O = Na_2SO_4 + 10H_2O$$

The temperature of 32·5°, it was learned, constituted a *transition point* for the decahydrate and anhydrous salt plus water; decomposition of the hydrated salt occurring above this temperature, combination of the anhydrous salt and water below it.

Analogous phenomena are met with in systems constituted of two salts and water in which the formation of double salts can take place. Thus, for example, if *d*-sodium potassium tartrate is heated to above 55°, apparent partial fusion occurs, and the two single salts, *d*-sodium tartrate and *d*-potassium tartrate, are deposited, the change which occurs being represented by the equation—

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[1] *Zeitschr. physikal. Chem.*, 1900, **36**. 168.

[2] For a discussion of these systems, see van't Hoff, *Bildung und Spaltung von Doppelsalzen* (Leipzig, 1897).

$$4NaKC_4O_6H_4,4H_2O = 2Na_2C_4O_6H_4,2H_2O + 2K_2C_4O_6H_4\tfrac{1}{2}H_2O + 11\,H_2O$$

On the other hand, if sodium and potassium tartrates are mixed with water in the proportions shown on the right side of the equation, the system will remain partially liquid so long as the temperature is maintained above 55° (in a closed vessel to prevent loss of water), but on allowing the temperature to fall below this point, complete solidification will ensue, owing to the formation of the hydrated double salt. Below 55°, therefore, the hydrated double salt is the stable system, while above this temperature the two single salts plus saturated solution are stable.[1]

A similar behaviour is found in the case of the double salt copper dipotassium chloride ($CuCl_2,2KCl,2H_2O$ or $CuK_2Cl_4,2H_2O$).[2] When this salt is heated to 92°, partial liquefaction occurs, and the original blue plate-shaped crystals give place to brown crystalline needles and white cubes; while on allowing the temperature to fall, re-formation of the blue double salt ensues. The temperature 92° is, therefore, a transition point at which the reversible reaction—

$$CuK_2Cl_4,2H_2O \rightleftarrows CuKCl_3 + KCl + 2H_2O$$

takes place.

The decomposition of sodium potassium tartrate, or of copper dipotassium chloride, differs in so far from that of Glauber's salt that *two* new solid phases are formed; and in the case of copper dipotassium chloride, one of the decomposition products is itself a double salt.

In the two examples of double salt decomposition which have just been mentioned, sufficient water was yielded to cause a partial liquefaction; but other cases are known where this is not so. Thus, when copper calcium acetate is heated to a temperature of 75°, although decomposition of the double salt into the two single salts occurs as represented by the equation[1]—

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[1] *Van Leeuwen, Zeitschr. physikal. Chem.*, 1897, 23. 35.

[2] *Meyerhoffer, Zeitschr. physikal. Chem.*, 1889, 3. 336; 1890, 5. 97.

$$CuCa(C_2H_3O_2)_4,8H_2O = Cu(C_2H_3O_2)_2,H_2O + Ca(C_2H_3O_2)_2,H_2O + 6H_2O$$

the amount of water split off is insufficient to give the appearance of partial fusion, and, therefore, only a change in the crystals is observed.

The preceding examples, in which decomposition of the double salt was effected by a rise of temperature, were chosen for first consideration as being more analogous to the case of Glauber's salt; but not a few examples are known where the reverse change takes place, formation of the double salt occurring *above* the transition point, and decomposition into the constituent salts below it. Instances of this behaviour are found in the case of the formation of astracanite from sodium and magnesium sulphates, and of sodium ammonium racemate from the two sodium ammonium tartrates, to which reference will be made later. Between these various systems, however, there is no essential difference; and whether decomposition or formation of the double salt occurs at temperatures above the transition point, will of course depend on the heat of change at that point. For, in accordance with van't Hoft's law of movable equilibrium (p. 56), that change will take place at the higher temperature which is accompanied by an absorption of heat. If, therefore, the formation of the double salt from the single salts is accompanied by an absorption of heat, the double salt will be formed from the single salts on raising the temperature; but if the reverse is the case, then the double salt on being heated will decompose into the constituent salts.[2]

In those cases, now, which have so far been studied, the change at the transition point is accompanied by a taking up or a splitting off of water; and *in such cases the general rule can be given, that if the water of crystallization of the two constituent*

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[1] Reicher, *Zeitschr. physikal. Chem.*, 1887, **1.** 220.

[2] For other examples of the formation and decomposition of double salts at a transition point, the reader is referred to the work by van't Hoff, already cited, on the *Bildung und Spaltung von Doppelsalzen;* or to Bancroft, *Phase Rule*, p. 180.

salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature (*e.g.* astracanite from sodium and magnesium sulphates); *but if the double salt contains more water of crystallization than the two single salts, increase of temperature will effect the decomposition of the double salt.* When we seek for the connection between this rule and the law of van't Hoff, it is found in the fact that the heat effect involved in the hydration or dehydration of the salts is much greater than that of the other changes which occur, and determines, therefore, the sign of the total heat effect.[1]

Vapour Pressure. Quintuple Point.—In the case of Glauber's salt, we saw that at a certain temperature the vapour pressure curve of the hydrated salt cut that of the saturated solution of anhydrous sodium sulphate. That point, it will be remembered, was a quadruple point at which the four phases sodium sulphate decahydrate, anhydrous sodium sulphate, solution, and vapour, could co-exist; and was also the point of intersection of the curves for four univariant systems. In the case of the formation of double salts, similar relationships are met with; and also certain differences, due to the fact that we are now dealing with systems of three components. Two cases will be chosen here for brief description, one in which formation, the other in which decomposition of the double salt occurs with rise of temperature.

On heating a mixture of sodium sulphate decahydrate and magnesium sulphate heptahydrate, it is found that at 22° partial liquefaction occurs with formation of astracanite. At this temperature, therefore, there can coexist the five phases—

$$Na_2SO_4,10H_2O;\ MgSO_4,7H_2O;\ Na_2Mg(SO_4)_2,4H_2O;$$
$$\text{solution; vapour.}$$

This constitutes, therefore, a *quintuple point;* and since there are three components present in five phases, the system is invariant. This point, also, will be the point of intersection of curves for five univariant systems, which, in this case, must each be composed of four phases. These systems are—

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[1] Bancroft, *Phase Rule*, p. 183.

I. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; vapour.

II. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; solution; vapour.

III. $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

IV. $Na_2SO_4,10H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

V. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution.

On representing the vapour pressures of these different systems graphically, a diagram is obtained such as is shown in Fig. 93,[1] the curves being numbered in accordance with the above list. When the system I. is heated, the vapour pressure increases until at the quintuple point the liquid phase (solution) is formed, and it will then depend on the relative amounts of the different phases whether on further heating there is formed system III., IV., or V. If either of the first two is produced, we shall obtain the vapour pressure of the solutions saturated with respect to both double salt and one of the single salts; while if the vapour phase disappears, there will be obtained the pressure of the condensed systems formed of double salt, two single salts and solution. This curve, therefore, indicates the *change of the transition point with pressure;* and since in the ordinary determinations of the transition point in open vessels, we are in reality dealing with condensed systems under the pressure of 1 atm., it will be evident that the transition point does not accurately coincide with the quintuple point (at which the system is under the pressure of its own vapour). As in the case of other condensed systems, however, pressure has only a slight influence on the temperature of the transition point. Whether or not pressure raises or lowers the transition point will depend on whether transformation is accompanied by an increase or

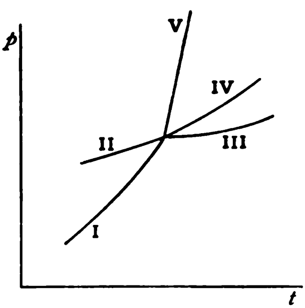

FIG. 93.

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[1] Roozeboom, *Zeitschr. physikal.* Chem., 1888, 2. 514.

diminution of volume (theorem of Le Chatelier, p. 56). In the case of the formation of astracanite, expansion occurs, and the transition point will therefore be raised by increase of pressure. Although measurements have not been made in the case of this system, the existence of such a curve has been experimentally verified in the case of copper and calcium acetates and water (v. *infra*).

The vapour pressure diagram in the case of copper calcium acetate and water (Fig. 94), is almost the reverse of that already discussed. In this case, the double salt decomposes on heating, and the decomposition is accompanied by a contraction. Curve I. is the vapour pressure curve for double salt, two single salts (p. 252), and vapour; curves II. and III. give the vapour pressures of solutions saturated with respect to double salt and one of the single salts; curve IV. is the curve of pressures for the solutions saturated with respect to the two single salts; while curve V. again represents the change of the transition point with pressure. On examining this diagram, it is seen that whereas astracanite could exist both above and below the quintuple point, copper calcium acetate can exist only *below* the quintuple point. This behaviour is found only in those cases in which the double salt is decomposed by rise of temperature, and where the decomposition is accompanied by a diminution of volume.[1]

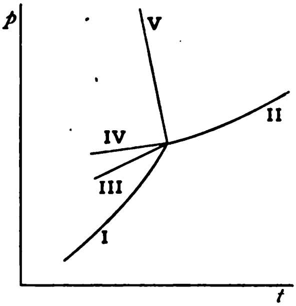

FIG. 94.

As already mentioned, the decomposition of copper calcium acetate into the single salts and saturated solution is accompanied by a contraction, and it was therefore to be expected that increase of pressure would *lower* the transition point. This expectation of theory was confirmed by experiment, for van't Hoff and Spring found that although the transition point under atmospheric pressure is about 75°, decomposition of the double salt took place even at the ordinary temperature when the pressure was increased to 6000 atm.[1]

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[1] *Roozeboom, Zeitschr. physikal. Chem.*, 1887, 1. 227.

Solubility Curves at the Transition Point.—At the transition point, as has already been shown, the double salt and the two constituent salts can exist in equilibrium with the same solution. The transition point, therefore, must be the point of intersection of two solubility curves; the solubility curve of the double salt and the solubility curve of the mixtures of the two constituent salts. It should be noted here that we are not dealing with the solubility curves of the single salts separately, for since the systems are composed of three components, a single solid phase can, at a given temperature, be in equilibrium with solutions of different composition, and two solid phases in contact with solution (and vapour) are therefore necessary to give an univariant system. The same applies, of course, to the solubility of the double salt; for a double salt also constitutes a single phase, and can therefore exist in equilibrium with solutions of varying composition. If, however, we make the restriction (which we do for the present) that the double salt is not decomposed by water, then the solution will contain the constituent salts in the same relative proportions as they are contained in the double salt, and the system may therefore be regarded as one of *two* components, viz. double salt and water. In this case one solid phase is sufficient, with solution and vapour, to give an univariant system; and at a given temperature, therefore, the solubility will have a perfectly definite value.

Since in almost all cases the solubility is determined in open vessels, we shall in the following discussion consider that the vapour phase is absent, and that the system is under a constant pressure, that of the atmosphere. With this restriction, therefore, four phases will constitute an invariant system, three phases an univariant, and two phases a bivariant system.

It has already been learned that in the case of sodium sulphate and water, the solubility curve of the salt undergoes a sudden change in direction at the transition point, and that this is accompanied by a change in the solid phase in equilibrium with the solution. The same behaviour is also found the case of double salts. To illustrate this, we shall briefly iscuss the solubility relations of a few double salts, beginning with one of the simplest cases, that of the formation of rubidium acemate from *d*- and *l*-rubidium tartrates. The solubilities are represented diagrammatically in Fig. 95, the numerical data being contained in the following table, in which the solubility is expressed as the number of gram-molecules $Rb_2C_4H_4O_6$ in 100 gm.-molecules of water.[1]

---

[1] *Zeitschr. physikal. Chem.*, 1887, **1**. 227.

Temperature.	Solubility of tartrate mixture.	Solubility of racemate.
25°	13·03	10·91
35°	—	12·63
40·4°	—	13·48
40·7°	13·46	—
54°	13·83	—

In Fig. 95 the curve AB represents the solubility of the racemate, while A′BC represents the solubility of the mixed tartrates. Below the transition point, therefore, the solubility of the racemate is less than that of the mixed tartrates. The solution, saturated with respect to the latter, will be supersaturated with respect to the racemate; and if a nucleus of this is present, racemate will be deposited, and the mixed tartrates, if present in equimolecular amounts, will ultimately entirely disappear, and only racemate will be left as solid phase. The solution will then have the composition represented by a point on the curve AB. Conversely, above the transition point, the saturated solution of the *racemate* would be supersaturated with respect

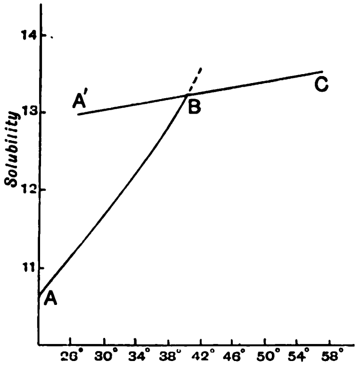

FIG. 95.

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[1] *Van't Hoff* and Müller, *Ber.*, 1898, 31. 2206.

to the two tartrates, and transformation into the latter would ensue. If, therefore, a solution of equimolecular proportions of *d*- and *l*-rubidium tartrates is allowed to evaporate at a temperature above 40°, a mixture of the two tartrates will be deposited; while at temperatures below 40° the racemate will separate out.

Similar relationships are met with in the case of *d*- and *l*-sodium ammonium tartrate and sodium ammonium racemate; but in this case the racemate is the stable form in contact with solution above the transition point (27°).[1] Below the transition point, therefore, the solubility curve of the mixed tartrates will lie below the solubility curve of the racemate. Below the transition point, therefore, sodium ammonium racemate will break up in contact with solution into a mixture of *d*- and *l*-sodium ammonium tartrates. At a higher temperature, 35°, sodium ammonium racemate undergoes decomposition into sodium racemate and ammonium racemate.[2]

The behaviour of sodium ammonium racemate is of interest from the fact that it was the first racemic substance to be resolved into its optically active forms by a process of crystallization. On neutralizing a solution of racemic tartaric acid, half with soda and half with ammonia, and allowing the solution to evaporate, Pasteur[3] obtained a mixture of *d*- and *l*-sodium ammonium tartrates. Since Pasteur was unaware of the existence of a transition point, the success of his experiment was due to the happy chance that he allowed the solution to evaporate at a temperature below 27°; for had he employed a temperature above this, separation of the racemate into the two enantiomorphous forms would not have occurred. For this reason the attempt of Staedel to perform the same resolution met only with failure.[4]

Decomposition of the Double Salt by Water.—In the two as a perfectly definite position, depending only on the nature f the three components.

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[1] Van't Hoff and van Deventer, *Zeitschr. physikal. Chem.*, 1887, 1. 165.

[2] For a full discussion of the solubility relations of sodium ammonium racemate, see van't Hoff, *Bildung und Spaltung von Doppelsalzen*, p. 81.

[3] *Annales chim. phys.*, 1848 [3], 24. 442.

[4] See Van't Hoff and van Deventer, Zeitschr. physikal. Chem., 1887, 1. 165.

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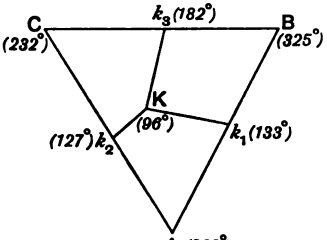

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Tin, 232°	—	37	63	Pb—Sn, 182°

Percentage composition of ternary eutectic mixture.			Temperature of ternary eutectic point.
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[1] Charpy, *Compt. rend.*, 1898, **126**. 1569. Compare the curves for the system KNO$_3$—NaNO$_3$—LiNO$_3$ (H. R. Carveth, *Journ. Physical Chem.*, 1898, **2**. 209). Also alloys of Pb—Sn—Bi (E. S. Shepherd, *Journ. Physical Chem.*, 1902, **6**. 527).

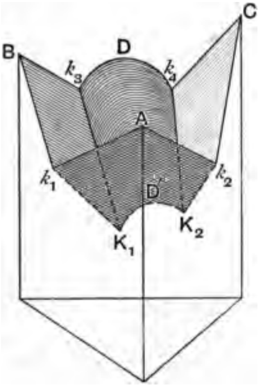

FIG. 92.

The particular point, now, to which it is desired to draw attention is this. Suppose the ternary eutectic curves projected on a plane parallel to the face of the prism containing B and C, *i.e.* suppose the concentrations of the two components B and C, between which interaction can occur, expressed in terms of a constant amount of the third component A,[1] curves will then be obtained which are in every respect analogous to the freezing point curves of binary systems. Thus, suppose the eutectic curves k_1K and k_2K in Fig. 90 projected on the face BC of the prism, then evidently a curve will be obtained consisting of two branches meeting in an eutectic point. On the other hand, the projection of the ternary eutectic curves in Fig. 92 on the face BC of the prism, will give a curve consisting of three portions, as shown by the outline $k_1K_1K_2k_2$ in Fig. 92.

Various examples of this have been studied, and the following table contains some of the data for the system ethylene bromide (A), picric acid (B), and β-naphthol (C), obtained by Bruni.[2]

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[1] It should be remembered that in the triangular diagram a *line* parallel to one of the sides indicates, at a given temperature, a constant amount of the component represented by the opposite corner of the triangle; and, hence, points in a *plane*, parallel to one face of a right prism, will indicate for different temperatures, variation in the amounts of two components, but constancy in the amount of the third.

[2] *Gazzetta chim. ital.*, 1898, **28**. II. 520.

contains a relatively smaller amount of sodium sulphate than a pure solution of astracanite would; for in this case there would be equal molecular amounts of Na_2SO_4 and $MgSO_4$. A solution which is saturated with respect to astracanite alone, will contain more sodium sulphate than the solution saturated with respect to astracanite plus Glauber's salt, and the latter will therefore be deposited. From this, therefore, it is clear that if astracanite is brought in contact with water at about the transition point, it will undergo decomposition with separation of Glauber's salt (supersaturation being excluded).

This will perhaps be made clearer by considering Fig. 96. In this diagram the ordinates represent the ratio of sodium sulphate to magnesium sulphate in the solutions, and the abscissæ represent the temperatures. The line AB represents solutions saturated with respect to a mixture of the single salts (p. 260); BC refers to solutions in equilibrium with astracanite and magnesium sulphate; while BX represents the composition of solutions in contact with the solid phases astracanite and Glauber's salt. The values of the solubility are contained in the following table, and in that on p. 260, and are, as before, expressed in gm.-molecules of salt in 100 gm.-molecules of water.[1]

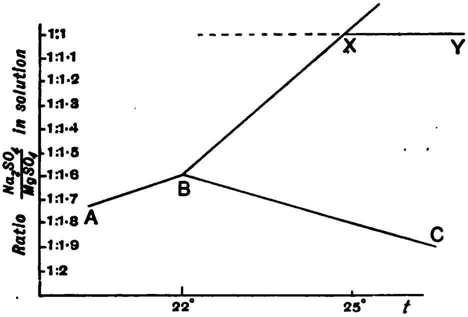

FIG. 96.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1888, 2. 518.

that temperature it occurs as a racemic mixed crystal[1] (*cf.* p. 217).

B. Equilibria at Higher Temperatures. Formation of Double Salts.—After having studied the relationships which are found in the neighbourhood of the freezing points of the components, we now pass to the discussion of the equilibria which are met with at higher temperatures. In this connection we shall confine the discussion entirely to the systems formed of two salts and water, dealing more particularly with those cases in which the water is present in relatively large amount and acts as solvent. Further, in studying these systems, one restriction must be made, viz. that the single salts are salts either of the same base or of the same acid; or are, in other words, capable of yielding a common ion in solution. Such a restriction is necessary, because otherwise the system would be one not of three but of four components.[2]

Transition Point.—As is very well known, there exist a number of hydrated salts which, on being heated, undergo apparent partial fusion; and in Chapter V. the behaviour of such hydrates was more fully studied in the light of the Phase Rule. Glauber's salt, or sodium sulphate decahydrate, for example, on being heated to a temperature of about 32·5°, partially liquefies, owing to the fact that the water of crystallization is split off and anhydrous sodium sulphate formed, as shown by the equation—

$$Na_2SO_4,10H_2O = Na_2SO_4 + 10H_2O$$

The temperature of 32·5°, it was learned, constituted a *transition point* for the decahydrate and anhydrous salt plus water; decomposition of the hydrated salt occurring above this temperature, combination of the anhydrous salt and water below it.

Analogous phenomena are met with in systems constituted of two salts and water in which the formation of double salts can take place. Thus, for example, if *d*-sodium potassium

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[1] *Zeitschr. physikal. Chem.*, 1900, **36**. 168.

[2] For a discussion of these systems, see van't Hoff, *Bildung und Spaltung von Doppelsalzen* (Leipzig, 1897).

K, however, the solution of the pure double salt is stable, for t is unsaturated with respect to double salt along with either f the single salts. At temperatures, then, above that at which the solution in contact with the double salt and the less soluble single salt, contains the single salts in the ratio in which they are present in the double salt, solution of the latter will take place without decomposition. *The range of temperature between that at which double salt can begin to be formed* (*the transition point*) *and that at which it ceases to be decomposed by water is called the transition interval.*[1] If the two single salts have identical solubility at the transition point, the transition interval diminishes to nought.

In those cases where the double salt is the stable form below the transition point, the transition interval will extend downwards to a lower temperature. Fig. 96 will then have the reverse form.

Summary.—With regard to double salts we have learned that their formation from and their decomposition into the single salts, is connected with a definite temperature, the *transition temperature.* At this transition temperature two vapour pressure curves cut, viz. a curve of dehydration of a mixture of the single salts and the solubility curve of the double salt; or the dehydration curve of the double salt and the solubility curve of the mixed single salts. The solubility curves, also, of these two systems intersect at the transition point, but although the formation of the double salt commences at the transition point, complete stability in contact with water may not be attained till some temperature above (or below) that point. *Only when the temperature is beyond the transition interval, will a double salt dissolve in water without decomposition* (e.g. *the alums*).

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[1] Meyerhoffer, *Zeitschr. physikal. Chem.*, 1890, **5.** 109.

CHAPTER XVI

ISOTHERMAL CURVES AND THE SPACE MODEL

In the preceding chapter we considered the changes in the solubility of double salts and of mixtures of their constituent salts with the temperature; noting, more especially, the relationships between the two systems at the transition point. It is now proposed to conclude the study of the three-component systems by discussing very briefly the solubility relations at constant temperature, or the isothermal solubility curves. In this way fresh light will be thrown on the change in the solubility of one component by the addition of another component, and also on the conditions of formation and stable existence of double salts in solution. With the help of these isothermal curves, also, the phenomena of crystallization at constant temperature—phenomena which have not only a scientific interest but also an important bearing on the industrial preparation of double salts—will be more clearly understood.[1]

A brief description will also be given of the method of representing the variation of the concentration of the two salts in the solution with the temperature.

Non-formation of Double Salts.—In Fig. 97 are shown the solubility curves of two salts, A and B, which at the given temperature do not form a double salt.[2] The ordinates represent the amount of A, the abscissæ the amount of B in a *constant amount* of the third component, the solvent. The

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[1] In connection with this chapter, see, more especially, van't Hoff, *Bildung und Spaltung von Doppelsalzen*, p. 3, *ff.*; Roozeboom, *Zeitschr. physikal Chem.*, 1892, **10.** 158; Bancroft, *Phase Rule*, p. 201; 209.

[2] The same restriction must be made here as was imposed in the preceding chapter, namely, that the two salts in solution give a common ion.

salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature (*e.g.* astracanite from sodium and magnesium sulphates); *but if the double salt contains more water of crystallization than the two single salts, increase of temperature will effect the decomposition of the double salt.* When we seek for the connection between this rule and the law of van't Hoff, it is found in the fact that the heat effect involved in the hydration or dehydration of the salts is much greater than that of the other changes which occur, and determines, therefore, the sign of the total heat effect.[1]

Vapour Pressure. Quintuple Point.—In the case of Glauber's salt, we saw that at a certain temperature the vapour pressure curve of the hydrated salt cut that of the saturated solution of anhydrous sodium sulphate. That point, it will be remembered, was a quadruple point at which the four phases sodium sulphate decahydrate, anhydrous sodium sulphate, solution, and vapour, could co-exist; and was also the point of intersection of the curves for four univariant systems. In the case of the formation of double salts, similar relationships are met with; and also certain differences, due to the fact that we are now dealing with systems of three components. Two cases will be chosen here for brief description, one in which formation, the other in which decomposition of the double salt occurs with rise of temperature.

On heating a mixture of sodium sulphate decahydrate and magnesium sulphate heptahydrate, it is found that at 22° partial liquefaction occurs with formation of astracanite. At this temperature, therefore, there can coexist the five phases—

$$Na_2SO_4,10H_2O;\ MgSO_4,7H_2O;\ Na_2Mg(SO_4)_2,4H_2O;$$
$$\text{solution; vapour.}$$

This constitutes, therefore, a *quintuple point;* and since there are three components present in five phases, the system is invariant. This point, also, will be the point of intersection of curves for five univariant systems, which, in this case, must each be composed of four phases. These systems are—

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[1] Bancroft, *Phase Rule*, p. 183.

I. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; vapour.

II. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; solution; vapour.

III. $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

IV. $Na_2SO_4,10H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution; vapour.

V. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution.

On representing the vapour pressures of these different systems graphically, a diagram is obtained such as is shown in Fig. 93,[1] the curves being numbered in accordance with the above list. When the system I. is heated, the vapour pressure increases until at the quintuple point the liquid phase (solution) is formed, and it will then depend on the relative amounts of the different phases whether on further heating there is formed system III., IV., or V. If either of the first two is produced, we shall obtain the vapour pressure of the solutions saturated with respect to both double salt and one of the single salts; while if the vapour phase disappears, there will be obtained the pressure of the condensed systems formed of double salt, two single salts and solution. This curve, therefore, indicates the *change of the transition point with pressure;* and since in the ordinary determinations of the transition point in open vessels, we are in reality dealing with condensed systems under the pressure of 1 atm., it will be evident that the transition point does not accurately coincide with the quintuple point (at which the system is under the pressure of its own vapour). As in the case of other condensed systems, however, pressure has only a slight influence on the temperature of the transition point. Whether or not pressure raises or lowers the transition point will depend on whether transformation is accompanied by an increase or

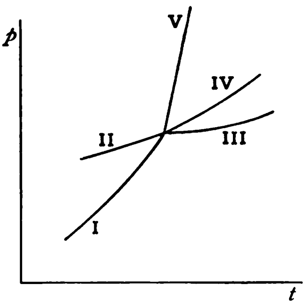

FIG. 93.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1888, **2**. 514.

tion of volume (theorem of Le Chatelier, p. 56). In e of the formation of astracanite, expansion occurs, and insition point will therefore be raised by increase of e. Although measurements have not been made in the this system, the existence of such a curve has been nentally verified in the case of copper and calcium s and water (v. *infra*).

vapour pressure diagram in the case of copper calcium and water (Fig. 94), is almost the reverse of that discussed. In this case, uble salt decomposes on , and the decomposition mpanied by a contraction. I. is the vapour pressure for double salt, two single . 252), and vapour; curves I III. give the vapour pressure of solutions saturated with to double salt and one of gle salts; curve IV. is the of pressures for the solu-aturated with respect to the two single salts; while curve in represents the change of the transition point with e. On examining this diagram, it is seen that whereas nite could exist both above and below the quintuple copper calcium acetate can exist only *below* the quintuple This behaviour is found only in those cases in which uble salt is decomposed by rise of temperature, and the decomposition is accompanied by a diminution of .[1]

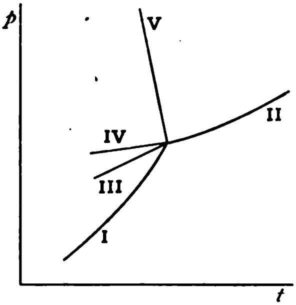

FIG. 94.

already mentioned, the decomposition of copper calcium into the single salts and saturated solution is accom- by a contraction, and it was therefore to be expected icrease of pressure would *lower* the transition point. xpectation of theory was confirmed by experiment, for Ioff and Spring found that although the transition point atmospheric pressure is about 75°, decomposition of the only with respect to the single salts, but also for the double salt in presence of the single salts.

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[1] Roozeboom, *Zeitschr. physikal. Chem.*, 1887, 1. 227.

We have just seen that by a change of temperature the two solubility curves, that for the two single salts and that for the double salt, were made to approach one another (*cf.* Figs. 99 and 100). In the previous chapter, however, we found that on passing the transition point to the region of stability for the double salt, the solution which is saturated for a mixture of the two constituent salts, is supersaturated for the double salt. In this case, therefore, point C must lie above the solubility curve of the pure double salt (Fig. 101), and a solution of the composition C, if brought in contact with double salt, will deposit the latter. If the single salts were also present, then as the double salt separated out, the single salts would pass into solution, because so long as the two single salts are present, the composition of the solution must remain unaltered. If one of the single salts disappear before the other, there will be left double salt plus A or double salt plus B, according to which was in excess; and the composition of the solution will be either that represented by D (saturated for double salt plus A), or that of the point F (saturated for double salt plus B).

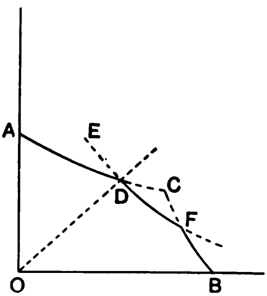

FIG. 101.

In connection with the isothermal represented in Fig. 101, it should be noted that at this particular temperature a solution saturated with respect to the pure double salt is no longer supersaturated for one of the single salts (point D); so that at the temperature of this isothermal the double salt is not decomposed by water. At this temperature, further, the boundary curve consists of three branches AD, DF, and FB, which give the composition of the solutions in equilibrium with pure A, double salt, and pure B respectively; while the points D and F represent solutions saturated for double salt plus A and double salt plus B.

On continuing to alter the temperature in the same direction

As before, the relative shifting of the solubility curves becomes more marked, as shown in Fig. 102. At the temperature of this isothermal, the solution saturated for the double salt now lies in a region of distinct unsaturation with respect to the single salts; and the double salt can now exist as solid phase in contact with solutions containing both relatively more of A (curve ED), and relatively more of B (curve DF), than is contained in the double salt itself.

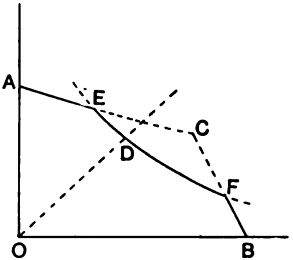

FIG. 102.

Transition Interval.—From what has been said, and from an examination of the isothermal diagrams, Figs. 99–102, it will be seen that by a variation of the temperature we can pass from a condition where the double salt is quite incapable of existing in contact with solution (supersaturation being excluded), to a condition where the existence of the double salt in presence of solution becomes possible; only in the presence, however, of one of the single salts (*transition point*, Fig. 100). A further change of temperature leads to a condition where the stable existence of the pure double salt in contact with solution just becomes possible (Fig. 101); and from this point onwards, pure saturated solutions of the double salt can be obtained (Fig. 102). *At any temperature, therefore, between that represented by Fig.* 100, *and that represented by Fig.* 101, *the double salt undergoes partial decomposition, with deposition of one of the constituent salts.* The temperature range between the transition point and the temperature at which a stable saturated solution of the pure double salt just begins to be possible, is known as he *transition interval* (p. 262). As the figures show, the transiion interval is limited on the one side by the transition temperature, and on the other by the temperature at which the olution saturated for double salt and the less soluble of the ingle salts, contains the component salts in the same ratio as hey are present in the double salt. The greater the difference n the solubility of the single salts, the larger will be the ansition interval.

Isothermal Evaporation.—The isothermal solubility curves are of great importance for obtaining an insight into the behaviour of a solution when subjected to isothermal evaporation. To simplify the discussion of the relationships found here, we shall still suppose that the double salt contains the single salts in equimolecular proportions; and we shall, in the first instance, suppose that the unsaturated solution with which we commence, also contains the single salts in the same ratio. The composition of the solution must, therefore, be represented by some point lying on the line OD, the bisectrix of the right angle.

If an unsaturated solution of the two single salts in equimolecular proportion (*e.g.* point *x*, Fig. 103) is evaporated at a temperature at which the formation of double salt is impossible, the component A, the solubility curve of which is cut by the line OD, will first separate out; the solution will thereby become richer in B. On continued evaporation, more A will be deposited, and the composition of the solution will change until it attains the composition represented by the point C, when both A and B will be deposited, and the composition of the solution will remain unchanged. The result of evaporation will therefore be a mixture of the two components.

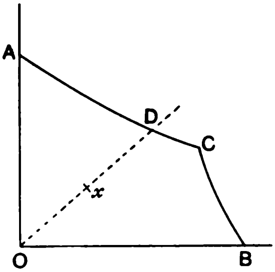

FIG. 103.

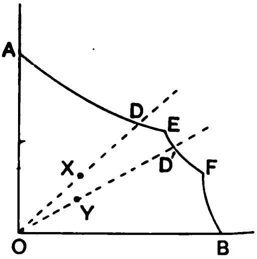

FIG. 104.

If the formation of double salt is possible, but if the temperature lies within the transition interval, the relations will be represented by a diagram like Fig. 104. Isothermal evaporation of the solution X will lead to the deposition of the component A, and the composition of the solution will alter in the irection DE; at the latter point the double salt will be formed, nd the composition of the solution will remain unchanged so ong as the two solid phases are present. As can be seen from the diagram, however, the solution in E contains less of comonent A than is contained in the double salt. Deposition of the double salt at E, therefore, would lead to a relative decrease n the concentration of A in the solution, and to counterbalance his, *the salt which separated out at the commencement must reissolve.*

Since the salts were originally present in equimolecular proportions, the final result of evaporation will be the pure double salt. If when the solution has reached the point E the salt A which had separated out is removed, double salt only will be left as solid phase. At a given temperature, however, a single solid phase can exist in equilibrium with solutions of different composition. If, therefore, isothermal evaporation s continued after the removal of the salt A, double salt will be deposited, and the composition of the solution will change in the direction EF. At the point F the salt B will separate out, and on evaporation both double salt and the salt B will be deposited. In the former case (when the salt A disappears on evaporation) we are dealing with an *incongruently saturated solution;* but in the latter case, where both solid phases continue to be deposited, the solution is said to be *congruently saturated.*[1]

A "congruently saturated solution" is one from which the solid phases are continuously deposited during isothermal evaporation to dryness, whereas in the case of "incongruently saturated solutions," at least one of the solid phases disappears during the process of evaporation.

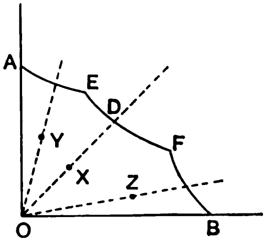

FIG. 105.

Lastly, if the temperature lies outide the transition interval, isothermal evaporation of an unsaturated solution of the composition X (Fig. 105) will lead to the deposition of pure double salt from beginning to end. If a solution of the composition Y is evaporated, the component A will first be deposited and the composition of the solution will alter in the direction of E, at which point double salt will separate out. Since the solution at this point contains relatively more of A than is present in the double salt, both the double salt and the single salt A will be deposited on continued evaporation, in order that the composition of the solution shall remain unchanged. In the case of solution Z, first component B and afterwards the double salt will be deposited. The result will, therefore, be a mixture of double salt and the salt B (congruently saturated solutions).

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[1] Meyerhoffer, *Ber.*, 1897, **30.** 1809.

Crystallization of Double Salt from Solutions containing Excess of one Component.—One more case of isothermal crystallization may be discussed. It is well known that a double salt which is decomposed by pure water can nevertheless be obtained pure by crystallization from a solution containing excess of one of the single salts (*e.g.* in the case of carnallite). Since the double salt is partially decomposed by water, the temperature of the experiment must be within the transition interval, and the relations will, therefore, be represented by a diagram like Fig. 104. If, now, instead of starting with an unsaturated solution containing the single salts in equimolecular proportions, we commence with one in which excess of one of the salts is present, as represented by the point Y, isothermal evaporation will cause the composition to alter in the direction YD′, the relative amounts of the single salts remaining the same throughout. When the composition of the solution reaches the point D′, pure double salt will be deposited. The separation of double salt will, however, cause a relative decrease in the concentration of the salt A, and the composition of the solution will, therefore, alter in the direction D′F. If the evaporation is discontinued before the solution has attained the composition F, only double salt will have separated out. Even within the transition interval, therefore, pure double salt can be obtained by crystallization, provided the original solution has a composition represented by a point lying between the two lines OE and OF. Since, as already nown, the composition of the solution alters on evaporation n the direction EF, it will be best to employ a solution having composition near to the line OE.

Formation of Mixed Crystals.—If the two single salts A nd B do not crystallize out pure from solution, but form an nbroken series of mixed crystals, it is evident that an invariant ystem cannot be produced. The solubility curve will therefore e continuous from A to B; the liquid solutions of varying omposition being in equilibrium with solid solutions also of arying composition. If, however, the series of mixed crystals s not continuous, there will be a break in the solubility curve t which two solid solutions of different composition will be in quilibrium with liquid solution. This, of course, will constitute n invariant system, and the point will correspond to the point C in Fig. 103. A full discussion of these systems would, however, lead us too far, and the above indication of the behaviour must suffice.[1]

Application to the Characterization of Racemates.—The orm of the isothermal solubility curves is also of great value or determining whether an inactive substance is a racemic compound or a conglomerate of equal proportions of the optical antipodes.[2]

As has already been pointed out, the formation of racemic compounds from the two enantiomorphous isomerides, is nalogous to the formation of double salts. The isothermal olubility curves, also, have a similar form. In the case of the atter, indeed, the relationships are simplified by the fact that the two enantiomorphous forms have identical solubility, and he solubility curves are therefore symmetrical to the line bisectng the angle of the co-ordinates. Further, with the exception f the partially racemic compounds to be mentioned later, there s no transition interval.

In Fig. 106, are given diagrammatically two isothermal solubility curves for optically active substances. From what has been said in the immediately preceding pages, the figure ought really to explain itself. The upper isothermal *acb* represents the solubility relations when the formation of a racemic compound is excluded, as, *e.g.* in the case of *d*- and *l*-rubidium tartrates above the transition point (p. 257). The solution at the point *c* is, of course, inactive, and *is unaffected by addition of either the* d- *or* l- *form.* The lower isothermal, on the other hand, would be obtained at a temperature at which the racemic compound could be formed. The curve *a'e* is the solubility curve for the *l*- form; *b'f*, that for the *d*- form; and *edf*, that for the racemic compound in presence of solutions of varying concentration. The point *d* corresponds to saturation for the pure racemic compound.

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[1] Bancroft, *Phase Rule*, p. 203; Roozeboom, *Zeitschr. physikal. Chem.*, 891, **8.** 504, 531; Stortenbeker, *ibid.*, 1895, **17.** 643; 1897, **22.** 60; 900, **34.** 108.

[2] Roozeboom, *Zeitschr. physikal. Chem.*, 1899, **28.** 494; *Ber.*, 1899, **32.** 37.

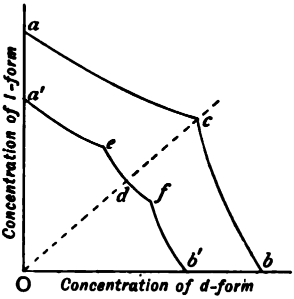

FIG. 106.

From these curves now, it will be evident that it will be possible, in any given case, to decide whether or not an inactive body is a mixture or a racemic compound. For this purpose, two solubility determinations are made, first with the inactive material alone (in excess), and then with the inactive material plus excess of one of the optically active forms. If we are dealing with a mixture, the two solutions thus obtained will be identical; both will have the composition corresponding to the point *c*, and will be inactive. If, however, the inactive material is a racemic compound, then two different solutions will be obtained; namely, an inactive solution corresponding to the point *d* (Fig. 106), and an *active* solution corresponding either to *c* or to *f*, according to which enantiomorphous form was added.

Partially racemic compounds.[1] In this case we are no

As, for instance, strychnine racemate, a compound of racemic acid with the *optically active* strychnine. This would be resolved into strychnine *d*-tartrate and strychnine *l*-tartrate, which are not enantiomorphous forms.

longer dealing with enantiomorphous forms, and the solubility of the two oppositely active isomerides is no longer the same. The symmetry of the solubility curves therefore disappears, and a figure is obtained which is identical in its general form with that found in the case of ordinary double salts (Fig. 107). In this case there is a transition interval.

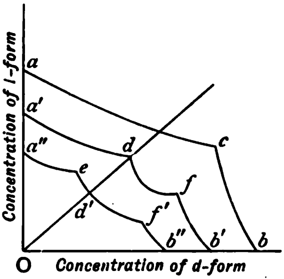

FIG. 107.

The curves *acb* belong to a temperature at which the partially racemic compound cannot be formed; *a'dfb'*, to the temperature at which the compound just begins to be stable in contact with water, and *a''ed'f'b''* belongs to a temperature at which the partially racemic compound is quite stable in contact with water. Suppose now solubility determinations, made in the first case with the original material alone, and then with the original body plus each of the two compounds, formed from the enantiomorphous substances separately, then if the original body was a mixture, identical solutions will be obtained in all three cases (point *c*); if it was a partially racemic compound, three different solutions (*e*, *d'*, and *f'*) will be obtained if the temperature was outside the transition interval, and two solutions, *d* and *f*, if the temperature belonged to the transition interval.

Representation in Space.

Space Model for Carnallite.—Interesting and important as the isothermal solubility curves are, they are insufficient for the purpose of obtaining a clear insight into the complete behaviour of the systems of two salts and water. A short description will, therefore, be given here of the representation in space of the solubility relations of potassium and magnesium chlorides, and of the double salt which they form, carnallite.[1]

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[1] Van't Hoff and Meyerhoffer, *Zeitschr. physikal. Chem.*, 1898, 27. 75; *899, 30. 86. Fig.* 108 is taken from the latter paper.

Fig. 108 is a diagrammatic sketch of the model for carnallite looked at sideways from above. Along the X-axis is measured the concentration of magnesium chloride in the solution; along the Y-axis, the concentration of potassium chloride; while along the T-axis is measured the temperature. The three axes are at right angles to one another. The XT-plane, therefore, contains the solubility curve of magnesium chloride; the YT-plane, the solubility curve of potassium chloride, and in the space between the two planes, there are represented the composition of solutions containing both magnesium and potassium chlorides. Any *surface* between the *two* planes will represent the various solutions in equilibrium with only one solid phase, and will therefore indicate the are

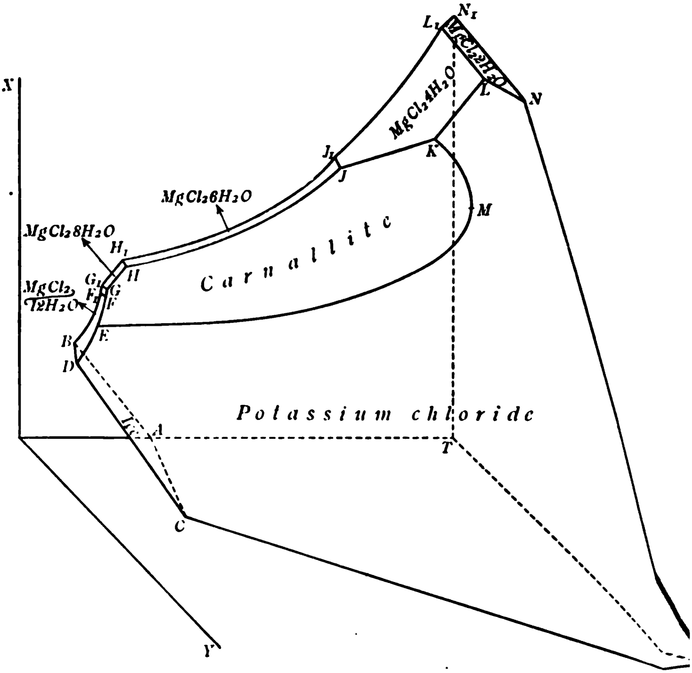

FIG. 108.

or field of existence of bivariant ternary systems. A *line* or *curve* formed by the intersection of two surfaces will represent solutions in equilibrium with two solid phases (viz. those belonging to the intersecting surfaces), and will show the conditions for the existence of univariant systems. Lastly, *points* formed by the intersection of three surfaces will represent invariant systems, in which a solution can exist in equilibrium with three solid phases (viz. those belonging to the three surfaces).

We shall first consider the solubility relations of the single salts. The complete equilibrium curve for magnesium chloride and water is represented in Fig. 108 by the series of curves ABF_1 G_1 H_1 J_1 L_1 N_1. AB is the freezing-point curve of ice in contact with solutions containing magnesium chloride, and B is the cryohydric point at which the solid phases ice and $MgCl_2,12H_2O$ can co-exist with solution. BFG is the solubility curve of magnesium chloride dodecahydrate. This curve shows a point of maximum temperature at F_1, and a retroflex portion F_1G_1. The curve is therefore of the form exhibited by calcium chloride hexahydrate, or the hydrates of ferric chloride (Chapter VIII.). G_1 is a transition point at which the solid phase changes from dodecahydrate to octahydrate, the solubility of which is represented by the curve G_1H_1. At H_1 the octahydrate gives place to the hexahydrate, which is the solid phase in equilibrium with the solutions represented by the curve H_1J_1. J_1 and L_1 are also transition points at which the solid phase undergoes change, in the former case from hexahydrate to tetrahydrate; and in the latter case, from tetrahydrate to dihydrate. The complete curve of equilibrium for magnesium chloride and water is, therefore, somewhat complicated, and is a good example of the solubility curves obtained with salts capable of forming several hydrates.

The solubility curve of potassium chloride is of the simplest form, consisting only of the two branches AC, the freezing-point curve of ice, and CO, the solubility curve of the salt. C is the *cryohydric* point. This point and the two curves lie in the *YT-plane.*

On passing to the ternary systems, the composition of the solutions must be represented by points or curves situated *between* the two planes. We shall now turn to the consideration of these. BD and CD are ternary eutectic curves (p. 276). They give the composition of solutions in equilibrium with ice and magnesium chloride dodecahydrate (BD), and with ice and potassium chloride (CD). D is a *ternary cryohydric point.* If the temperature is raised and the ice allowed to disappear, we shall pass to the solubility curve for $MgCl_2,12H_2O + KCl$ (curve DE). At E carnallite is formed and the potassium chloride disappears; EFG is then the solubility curve for $MgCl_2,12H_2O$ + carnallite ($KMgCl_3,6H_2O$). This curve also shows a point of maximum temperature (F) and a retroflex portion. GH and HJ represent the solubility curves of carnallite + $MgCl_2,8H_2O$ and carnallite + $MgCl_2,6H_2O$, G and H being transition points. JK is the solubility curve for carnallite + $MgCl_2,4H_2O$. At the point K we have the *highest temperature at which carnallite can exist with magnesium chloride in contact with solution.* Above this temperature decomposition takes place and potassium chloride separates out.

If at the point E, at which the two single salts and the double salt are present, excess of potassium chloride is added, the magnesium chloride will all disappear owing to the formation of carnallite, and there will be left carnallite and potassium chloride. The solubility curve for a mixture of these two salts is represented by EMK; a simple curve exhibiting, however, a temperature maximum at M. This maximum point corresponds with the fact that dry carnallite melts at this temperature with separation of potassium chloride. *At all temperatures above this point, the formation of double salt is impossible.* The retroflex portion of the curve represents solutions in equilibrium with carnallite and potassium chloride, but in which the ratio $MgCl_2 : H_2O$ is greater than in the double salt.

Throughout its whole course, *the curve EMK represents solutions in which the ratio of* $MgCl_2 : KCl$ *is greater than in the double salt.* As this is a point of some importance, it will be well, perhaps, to make it clearer by giving one of the isothermal curves, *e.g.* the curve for 10°, which is represented diagrammatically in Fig. 109. E and F here represent solutions saturated for carnallite plus magnesium chloride hydrate, and for carnallite plus potassium chloride. As is evident, the point F lies above the line representing equimolecular proportions of the salts (OD).

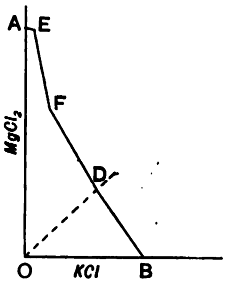

Fig. 109.

Summary and Numerical Data.—We may now sum up the different systems which can be formed, and give the numerical data from which the model is constructed.[1]

I. *Bivariant Systems.*

Solid phase.	Area of existence.
Ice	ABDC
KCl	CDEMKLNO
Carnallite	EFGHJKM
$MgCl_2,12H_2O$	BF_1G_1GFED
$MgCl_2,8H_2O$	G_1H_1HG
$MgCl_2,6H_2O$	H_1I_1IH
$MgCl_2,4H_2O$	I_1L_1LKI
$MgCl_2,2H_2O$	L_1N_1NL

II. *Univariant Systems.*—The different univariant systems have already been described. The course of the curves will be sufficiently indicated if the temperature and composition of he solutions for the different invariant systems are given.

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[1] Solid models constructed of plaster of Paris can be obtained from Max Kaehler and Martini, Berlin.

III.—*Invariant Systems—Binary and Ternary.*

Point.	Solid phases.	Temperature.	Composition of solution. G molecules of salt per 1000 g mol. water.
A	Ice	0°	—
B	Ice ; $MgCl_2,12H_2O$	−33·6°	49·2 $MgCl_2$
C	Ice ; KCl	−11·1°	59·4 KCl
D	Ice ; $MgCl_2,12H_2O$; KCl	−34·3°	43 $MgCl_2$; 3 KC
E	$MgCl_2,12H_2O$; KCl ; carnallite	−21°	66·1 $MgCl_2$; 4·9 K
F_1	$MgCl_2,12H_2O$	−16·4°	83·33 $MgCl_2$
F	$MgCl_2,12H_2O$; carnallite	−16·6°	Almost same as F ; tains small amount o
G_1	$MgCl_2,12H_2O$; $MgCl_2,8H_2O$	−16·8°	87·5 $MgCl_2$
G	$MgCl_2,12H_2O$; $MgCl_2,8H_2O$; carnallite	−16·9°	Almost same as G_1 contains small qu of KCl
H_1	$MgCl_2,8H_2O$; $MgCl_2,6H_2O$	−3·4°	99 $MgCl_2$
H	$MgCl_2,8H_2O$; $MgCl_2,6H_2O$; carnallite	ca. −3·4°	Almost same as H_1 contains small amo KCl
J_1	$MgCl_2,6H_2O$; $MgCl_2,4H_2O$	116·67°	161·8 $MgCl_2$
J	$MgCl_2,6H_2O$; $MgCl_2,4H_2O$; carnallite	115·7°	162 $MgCl_2$; 4 K
K	$MgCl_2\ 4H_2O$; KCl ; carnallite	152·5°	200 $MgCl_2$; 24 K
L_1	$MgCl_2,4H_2O$; $MgCl_2,2H_2O$	181°	238·1 $MgCl_2$
L	$MgCl_2,4H_2O$; $MgCl_2,2H_2O$; KCl	176°	240 $MgCl_2$; 41 K
M	Carnallite ; KCl	167·5°	166·7 $MgCl_2$; 41·7
[N_1	$MgCl_2,2H_2O$	186°	ca. 241 $MgCl_2$]
N	$MgCl_2,2H_2O$; KCl	186°	240 $MgCl_2$; 63 K
[O	KCl	186°	195·6 KCl]

With the help of the data in the preceding table and solid model it will be possible to state in any given case will be the behaviour of a system composed of magn chloride, potassium chloride and water. One or two dif cases will be very briefly described ; and the reader s have no difficulty in working out the behaviour under conditions with the help of the model and the numerica just given.

In the first place it may be again noted that at a temperature above 167·5° (point M) carnallite cannot exist. If, therefore, a solution of magnesium and potassium chlorides is evaporated at a temperature above this point, the result will be a mixture of potassium chloride and either magnesium chloride tetrahydrate or magnesium chloride dihydrate, according as the temperature is below or above 176°. The isothermal curve here consists of only two branches.

Further, reference has already been made to the fact that all points of the carnallite area correspond to solutions in equilibrium with carnallite, but in which the ratio of $MgCl_2$ to KCl is greater than in the double salt. A solution which is saturated with respect to double salt alone will be supersaturated with respect to potassium chloride. At all temperatures, therefore, carnallite is decomposed by water with separation of potassium chloride; hence all solutions obtained by adding excess of carnallite to water will lie on the curve EM. *A pure saturated solution of carnallite cannot be obtained.*

If an unsaturated solution of the two salts in equimolecular amounts is evaporated, potassium chloride will first be deposited, because the plane bisecting the right angle formed by the X and Y axes cuts the area for that salt. Deposition of potassium chloride will lead to a relative increase in the concentration of magnesium chloride in the solution; and on continued evaporation a point (on the curve EM) will be reached at which carnallite will separate out. So long as the two solid phases are present, the composition of the solution must remain unchanged. Since the separation of carnallite causes a decrease in the relative concentration of the potassium chloride in the solution, the portion of this salt which was deposited at the commencement must *redissolve*, and carnallite will be left on evaporating to dryness. (*Incongruently saturated solution.*)

Although carnallite is decomposed by pure water, it will be possible to crystallize it from a solution having a composition represented by any point in the carnallite area. Since during the separation of the double salt the relative amount of magnesium chloride increases, it is most advantageous to commence with a solution the composition of which is represented by a point lying just above the curve EM (cf. p. 272).

From the above description of the behaviour of carnallite in solution, the processes usually employed for obtaining potassium chloride will be readily intelligible.[1]

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[1] Instead of the present method of obtaining potassium chloride by decomposing carnallite with water, advantage might be taken of the fact that carnallite when heated to 168° undergoes decomposition with separation of three-fourths of the potassium chloride (van't Hoff, *Acht Vorträge über physikalische Chemie* 1902, p. 32).

CHAPTER XVII

SYSTEMS OF FOUR COMPONENTS

N the systems which have so far been studied, we have met with cases where two or three components could enter into combination; but in no case did we find double decomposition occurring. The reason of this is that in the systems previously tudied, in which double decomposition might have been possible, namely in those systems in which two salts acted as components, the restriction was imposed that either the basic or the acid constituent of these salts must be the same; a restriction imposed, indeed, for the very purpose of excluding double decomposition. Now, however, we shall allow this estriction to fall, thereby extending the range of study.

Hitherto, in connection with four-component systems, the attention has been directed solely to the study of aqueous olutions of salts, and more especially of the salts which occur n sea-water, *i.e.* chiefly, the sulphates and chlorides of magesium, potassium, and sodium. The importance of these nvestigations will be recognized when one recollects that by he evaporation of sea-water there have been formed the normous salt-beds at Stassfurt, which constitute at present the hief source of the sulphates and chlorides of magnesium and otassium. The investigations, therefore, are not only of reat geological interest as tending to elucidate the conditions nder which these salt-beds have been formed, but are of no ss importance for the industrial working of the deposits.

It is, however, not the intention to enter here into any etailed description of the different systems which have so far een studied, and of the sometimes very complex relationships met with, but merely to refer briefly to some points of more general import in connection with these systems.[1]

Reciprocal Salt-Pairs. Choice of Components.—When two salts undergo double decomposition, the interaction can be expressed by an equation such as

$$NH_4Cl + NaNO_3 = NaCl + NH_4NO_3$$

Since one pair of salts—$NaCl + NH_4NO_3$—is formed from the other pair—$NH_4Cl + NaNO_3$—by double decomposition, the two pairs of salts are known as *reciprocal salt-pairs.*[2] It is with systems in which the component salts form reciprocal salt-pairs that we have to deal here.

It must be noted, however, that the four salts formed by two reciprocal salt-pairs do not constitute a system of four, but only of *three* components. This will be understood if it is recalled that only so many constituents are taken as components as are necessary to *express* the composition of all the phases present (p. 12). It will be seen, now, that the composition of each of the four salts which can be present together can be expressed in terms of three of them. Thus, for example, in the case of NH_4Cl, $NaNO_3$, NH_4NO_3, $NaCl$, we can express the composition of NH_4Cl by $NH_4NO_3 + NaCl - NaNO_3$; or of $NaNO_3$ by $NH_4NO_3 + NaCl - NH_4Cl$. In all these cases it will be seen that negative quantities of one of the components must be employed; but that we have seen to be quite permissible (p. 12). The *number* of components is, therefore, three; but any three of the four salts can be chosen.

Since, then, two reciprocal salt-pairs constitute only three mponents or independently variable constituents, another mponent is necessary in order to obtain a four-component stem. As such, we shall choose water.

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[1] A very useful summary of the investigations carried out by van't Hoff and his pupils on the formation of the Stassfurt salt-beds is given by E. F. Armstrong, in the *Reports of the British Association for* 1901, p. 262.

[2] See especially Meyerhoffer, *Sitzungsber. Wien. Akad.*, 1895, **104**, II. *b*, 840; Meyerhoffer and Saunders, *Zeitschr. physikal. Chem.*, 1899, **28**. 453; **31**. 370. The investigation of the equilibria between reciprocal salt-pairs alone (three-component systems) is of great importance for the artificial preparation of minerals, as also in analytical chemistry for the proper understanding of the methods of conversion of insoluble systems into soluble by fusion (see Meyerhoffer, Zeitschr. physikal. Chem., 1901, **38**. 307).

Transition Point.—In the case of the formation of double lts from two single salts, we saw that there was a point—the *uintuple point*—at which five phases could coexist. This point e also saw to be a transition point, on one side of which the uble salt, on the other side the two single salts in contact ith solution, were found to be the stable system. A similar haviour is found in the case of reciprocal salt-pairs. The ur-component system, two reciprocal salt-pairs and water, can ve rise to an invariant system in which the six phases, four lts, solution, vapour, can coexist; the temperature at which is is possible constitutes a *sextuple point.* Now, this sex-ple point is also a transition point, on the one side of which e one salt-pair, on the other side the reciprocal salt-pair, is able in contact with solution.

The sextuple point is the point of intersection of the curves six univariant systems, viz. four solubility curves with three lid phases each, a vapour-pressure curve for the system : two ciprocal salt-pairs—vapour; and a transition curve for the ndensed system : two reciprocal salt-pairs—solution. If we mit the vapour phase and work under atmospheric pressure n open vessels), we find that the transition point is the point intersection of four solubility curves.

Just as in the case of three-component systems we saw that e presence of one of the single salts along with the double lt was necessary in order to give a univariant system, so in e four-component systems the presence of a third salt is ecessary as solid phase along with one of the salt-pairs. In e case of the reciprocal salt-pairs mentioned above, the transi-on point would be the point of intersection of the solubility rves of the systems with the following groups of salts as solid hases : Below the transition point : $NH_4Cl + NaNO_3 + NaCl$; $H_4Cl + NaNO_3 + NH_4NO_3$; above the transition point : $aCl + NH_4NO_3 + NaNO_3$; $NaCl + NH_4NO_3 + NH_4Cl$. From is we see that the two salts NH_4Cl and $NaNO_3$ would be le to exist together with solution below the transition point, but not above it. This transition point has not been determined.

Formation of Double Salts.—In all cases of four-component systems so far studied, the transition points have not been points at which one salt-pair passed into its reciprocal, but at which a double salt was formed. Thus, at 4·4° Glauber's salt and potassium chloride form glaserite and sodium chloride, according to the equation

$$2Na_2SO_4, 10H_2O + 3KCl = K_3Na(SO_4)_2 + 3NaCl + 20H_2O$$

Above the transition point, therefore, there would be $K_3Na(SO_4)_2$, NaCl and KCl; and it may be considered that at a higher temperature the double salt would interact with the potassium chloride according to the equation

$$K_3Na(SO_4)_2 + KCl = 2K_2SO_4 + NaCl$$

thus giving the reciprocal of the original salt-pair. This point has, however, not been experimentally realized.[1]

Transition Interval.—A double salt, we learned (p. 269), when brought in contact with water at the transition point undergoes partial decomposition with separation of one of the constituent salts; and only after a certain range of temperature (transition interval) has been passed, can a pure saturated solution be obtained. A similar behaviour is also found in the case of reciprocal salt-pairs. If one of the salt-pairs is brought in contact with water at the transition point, interaction will occur and one of the salts of the reciprocal salt-pair will be deposited; and this will be the case throughout a certain range of temperature, after which it will be possible to prepare a solution saturated only for the one salt-pair. In the case of ammonium chloride and sodium nitrate the lower limit of the transition interval is 5·5°, so that above this temperature and up to that of the transition point (unknown), ammonium chloride and sodium nitrate in contact with water would give rise to a third salt by double decomposition, in this case to sodium chloride.

Graphic Representation.—For the graphic representation ms of four components, four axes may be chosen inter- at a point like the edges of a regular octahedron (Fig. Along these different axes the equivalent molecular s of the different salts are measured.

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[1] See Meyerhoffer, *Zeitschr. physikal.* Chem., 1899, 28. 459.

represent a given system consisting of xB, yC, and zD iven amount of water (where B, C, and D represent ent molecular amounts of the salts), measure off on OB lengths equal to x and y respectively. The point of tion a (Fig. 110) represents a solution containing xB $(ab = x;\ ac = y)$. From a a line aP is drawn parallel and equal to z. P then represents the solution of the omposition.

is usual, however, not to employ the three-dimensional

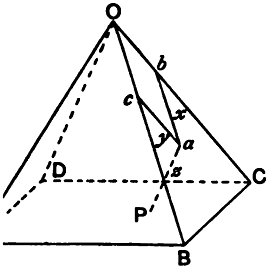

FIG. 110.

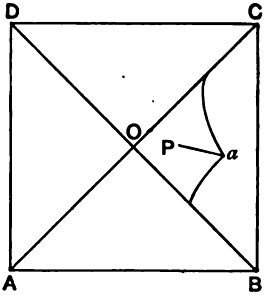

FIG. 111.

but its horizontal and vertical projections. Fig. 110, if ed on the base of the octahedron, would yield a diagram is shown in Fig. 111. The projection of the edges of ahedron form two axes at right angles and give rise to adrants similar to those employed for the representation ary solutions (p. 265). Here, the point a represents a solution saturated with respect to B and C; and aP, rnary solution in equilibrium with the same two salts as hases. Such a diagram represents the conditions of rium only for one definite temperature, and corresponds, re, to the isothermal diagrams for ternary systems). In such a diagram, since the temperature and

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[1] Löwenherz, *Zeitschr. physikal. Chem*, 1894, 13. 464.

pressure are constant (vessels open to the air), a surfa represent a solution in equilibrium with only one solid a line, a solution with two solid phases, and a point, equilibrium with three solid phases.

Example.—As an example of the complete isot

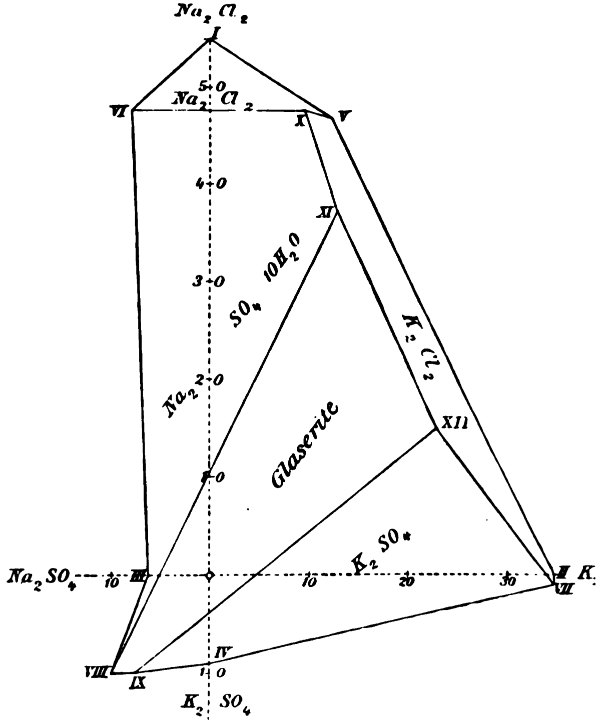

FIG. 112.

diagram, there may be given one representing the equili the system composed of water and the reciprocal s sodium sulphate—potassium chloride for the temperat (Fig. 112).[1] The amounts of the different salts are me along the four axes, and the composition of the solu expressed in equivalent gram-molecules per 1000 gram-molecules of water.[1]

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[1] Meyerhoffer and Saunders, *Zeitschr. physikal. Chem.*, 1899.

The outline of this figure represents four ternary solutions in which the component salts have a common acid or basic constituent; viz. sodium chloride—sodium sulphate, sodium sulphate—potassium sulphate, potassium sulphate—potassium chloride, potassium chloride—sodium chloride. These four sets of curves are therefore similar to those discussed in the previous chapter. In the case of sodium and potassium sulphate, a double salt, *glaserite* [$K_3Na(SO_4)_2$] is formed. Points VIII. and IX. represent solutions saturated with respect to glaserite and sodium sulphate, and glaserite and potassium sulphate respectively.

The lines which pass inwards from these boundary curves represent solutions containing three salts, but in contact with only two solid phases; and the points where three lines meet, or where three fields meet, represent solutions in equilibrium with three solid phases; with the phases, namely, belonging to the three concurrent fields.

If it is desired to represent a solution containing the salts say in the proportions, $51Na_2Cl_2$, $9{\cdot}5K_2Cl_2$, $3{\cdot}5K_2SO_4$, the difficulty is met with that two of the salts, sodium chloride and potassium sulphate, lie on opposite axes. To overcome this difficulty the difference $51 - 3{\cdot}5 = 47{\cdot}5$ is taken and measured off along the sodium chloride axis; and the solution is therefore represented by the point $47{\cdot}5Na_2Cl_2$, $9{\cdot}5K_2Cl_2$. In order, therefore, to find the amount of potassium sulphate present from such a diagram, it is necessary to know the total number of salt molecules in the solution. When this is known, it is only necessary to subtract from it the sum of the molecules of sodium and potassium chloride, and the result is equal to twice the number of potassium sulphate molecules. Thus, in the above example, the total number of salt molecules is 64. The number of molecules of sodium and potassium chloride is 57;

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[1] As the quantities of the salts are expressed in *equivalent* gram-molecules, the molecule of sodium and potassium chloride must be doubled in order to be equivalent to sodium sulphate and potassium sulphate.

64 − 57 = 7, and therefore the number of potassium sulphate molecules is 3·5.

Another method of representation employed is to indicate the amounts of only two of the salts in a plane diagram, and to measure off the total number of molecules along a vertical axis. In this way a solid model is obtained.

The numerical data from which Fig. 112 was constructed are contained in the following table, which gives the composition of the different solutions at 0°:—[1]

Point.	Solid phases.	Composition of solution in gram-mols. per 1000 gram-mols. water.				Total number of salt molecules.
		Na_2Cl_2.	K_2Cl_2.	Na_2SO_4.	K_2SO_4.	
I.	NaCl	55	—	—	—	55
II.	KCl	—	34·5	—	—	34·5
III.	$Na_2SO_4, 10H_2O$	—	—	6	—	6
IV.	K_2SO_4	—	—	—	9	9
V.	NaCl; KCl	46·5	12·5	—	—	59
VI.	NaCl; $Na_2SO_4, 10H_2O$	47·5	—	8	—	55·5
VII.	KCl; K_2SO_4	—	34·5	—	1	35·5
VIII.	Glaserite; $Na_2SO_4, 10H_2O$	—	—	10	10	20
IX.	Glaserite; K_2SO_4	—	—	7·5	10	17·5
X.	$Na_2SO_4, 10H_2O$; KCl; NaCl	51	9·5	—	3·5	64
XI.	$Na_2SO_4, 10H_2O$; KCl; glaserite	40·5	13	—	3·5	57
XII.	K_2SO_4; KCl; glaserite	18	23	—	3	44

From the aspect of these diagrams the conditions under which the salts can coexist can be read at a glance. Thus, for example, Fig. 112 shows that at 0° Glauber's salt and potassium chloride can exist together with solution; namely, in contact with solutions having the composition X—XI. This temperature must therefore be below the transition point of this salt-pair (p. 285). On raising the temperature to 4·4°, it is found that the curve VIII—XI moves so that the point XI coincides with point X. At this point, therefore, there will be *four* concurrent fields, viz. Glauber's salt, potassium chloride, glaserite and sodium chloride. But these four salts can coexist with solution only at the transition point; so that 4·4° is the transition temperature of the salt-pair: Glauber's salt—potassium chloride. At higher temperatures the line VIII—XI moves still further to the left, so that the field for Glauber's salt becomes entirely separated from the field for potassium chloride. This shows that at temperatures above the transition point the salt-pair Glauber's salt—potassium chloride cannot coexist in presence of solution.

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[1] Meyerhoffer and Saunders, *Zeitschr. physikal. Chem.*, 1899, 28, 479.

APPENDIX

‹PERIMENTAL DETERMINATION OF THE TRANSITION POINT

the purpose of determining the transition temperature, a :r of methods have been employed, and the most important se will be briefly described here. In any given case it is imes possible to employ more than one method, but all are ually suitable, and the values of the transition point obtained : different methods are not always identical. Indeed, a nce of several degrees in the value found may quite well [1] In each case, therefore, some care must be taken to select :thod most suitable for the purpose.

The Dilatometric Method.—Since, in the majority of cases, ›rmation at the transition point is accompanied by an :iable change of volume, it is only necessary to ascertain the rature at which this change of volume occurs, in order to ıine the transition point. For this purpose the *dilatometer* loyed, an apparatus which consists of a bulb with capillary ttached, and which constitutes a sort of large thermometer 13). Some of the substance to be examined is passed into lb A through the tube B, which is then sealed off. The rest bulb and a small portion of the capillary tube is then filled ›me liquid, which, of course, must be without chemical action substance under investigation. A liquid, however, may be ṿed which dissolves the substance, for, as we have seen), the transformation at the transition point is, as a rule, :ated by the presence of a solvent. On the other hand, the must not dissolve in the substance under examination, for nperature of transformation would be thereby altered.

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[1] :e Schwarz, *Beiträge zur Kenntnis der umkehrbaren Umwandlungen ·pher Korper* (Göttingen, 1892); or, Roozeboom, *Heterogen. Gleich-* , I. p. 125.

In using the dilatometer, two methods of procedure may be followed. According to the first method, the dilatometer containing the form stable at lower temperatures is placed in a thermostat, maintained at a constant temperature, until it has taken the temperature of the bath. The height of the meniscus is then read on a millimetre scale attached to the capillary. The temperature of the thermostat is then raised degree by degree, and the height of the meniscus at each point ascertained. If, now, no change takes place in the solid, the expansion will be practically uniform, or the rise in the level of the meniscus per degree of temperature will be practically the same at the different temperatures, as represented diagrammatically by the line AB in Fig. 114. On passing through the transition point, however, there will be a more or less sudden increase in the rise of the meniscus per degree (line BC) if the specific volume of the form stable at higher temperatures is greater than that of the original modification; thereafter, the expansion will again be uniform (line CD). Similarly, on cooling, contraction will at first be uniform and then at the transition point there will be a relatively large diminution of volume.

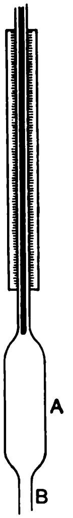

FIG. 113.

If, now, transformation occurred immediately the transition point was reached, the sudden expansion and contraction would take place at the same temperature. It is, however, generally found that there is a lag, and that with rising temperature the relatively large expansion does not take place until a temperature somewhat higher than the transition point; and with falling temperature the contraction occurs at a temperature somewhat below the transition point. This is represented in Fig. 114 by the lines BC and EF. The amount of lag will vary from case to case, and will

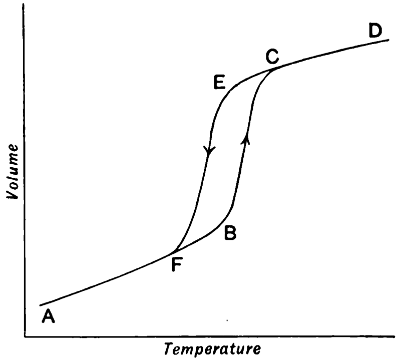

FIG. 114.

lso depend on the length of time during which the dilatometer s maintained at constant temperature.

As an example, there may be given the results obtained in the letermination of the transition point at which sodium sulphate and magnesium sulphate form astracanite (p. 259).[1] The dilatometer was charged with a mixture of the two sulphates.

Temperature.	Level of oil in capillary.	Rise per 1°.
15·6°	134	
16·6°	141	7
17·6°	148	7
18·6°	154	6
19·6°	161	7
20·6°	168	7
21·6°	241	73
22·6°	243	2
23·6°	251	8
24·6°	259	8

The transition point, therefore, lies about 21·6° (p. 259).

The second method of manipulation depends on the fact that, while above or below the transition point transformation of one form into the other can take place, at the transition point the two forms undergo no change. The bulb of the dilatometer is, therefore, charged with a mixture of the stable and metastable forms and a suitable liquid, and is then immersed in a bath at constant temperature. After the temperature of the bath has been acquired, readings of the height of the meniscus are made from time to time to ascertain whether expansion or contraction occurs. If expansion is found, the temperature of the thermostat is altered until a temperature is obtained at which a gradual contraction takes place. The transition point must then lie between these two temperatures; and by repeating the determinations it will be possible to reduce the difference between the temperatures at which expansion and contraction take place to, say, 1°, and to fix the temperature of the transition point, therefore, to within half a degree. By this method the transition point, for example, of sulphur was found to be 95·6° under a pressure of 4 atm.[2] The following are the figures obtained by Reicher, who used a mixture

---

[1] Van't Hoff and van Deventer, *Zeitschr. physikal. Chem.*, 1887, 1. 173.

[2] Reicher, *Zeitschr. für Krystallographie*, 1884, 8. 593.

of 1 part of carbon disulphide (solvent for sulphur) and 5 parts of turpentine as the measuring liquid.

TEMPERATURE 95·1°.

Time in minutes.	Level of liquid.
5	343·5
30	340·5
55	335·75
65	333

TEMPERATURE 96·1°.

Time in minutes.	Level of liquid.
5	342·75
30	354·75
55	360·5
60	361·5

TEMPERATURE 95·6°.

Time in minutes.	Level of liquid.
5	368·75
100	368
110	368·75

At a temperature of 95·1° there is a contraction, *i.e.* monoclinic sulphur passes into the rhombic, the specific volume of the former being greater than that of the latter. At 96·1°, however, there is expansion, showing that at this temperature rhombic sulphur passes into monoclinic; while at 95·6° there is neither expansion nor contraction. This is, therefore, the transition temperature; and since the dilatometer was sealed up to prevent evaporation of the liquid, the pressure within it was 4 atm.

II. Measurement of the Vapour Pressure.—In the preceding pages it has been seen repeatedly that the vapour pressures of the two systems undergoing reciprocal transformation become identical at the transition point (more strictly, at the triple or point), and the latter can therefore be determined by ning the temperature at which this identity of vapour e is established. The apparatus usually employed for this is the Bremer-Frowein tensimeter (p. 88).

ough this method has not as yet been applied to systems of nponent, it has been used to a considerable extent in the systems containing water or other volatile component. An of this has already been given in Glauber's salt (p. 137).

Solubility Measurements.—The temperature of the on point can also be fixed by means of solubility measure- for at that point the solubility of the two systems becomes l. Reference has already been made to several cases in his method was employed, *e.g.* ammonium nitrate (p. 110), 's salt (p. 132), astracanite and sodium and magnesium s (p. 260).

determinations of the solubility can be carried out in ways. One of the simplest methods, which also gives tly accurate results when the temperature is not high or e solvent is not very volatile, can be carried out in the g manner. The solid substance is finely powdered (in order lerate the process of solution), and placed in sufficient along with the solvent in a tube carefully closed by a opper; the latter is protected by a rubber cap, such as r finger-stall. The tube is then rotated in a thermostat, perature of which does not vary more than one or two f a degree, until saturation is produced. The solution is wn by means of a pipette to which a small glass tube, filled tton wool to act as a filter, is attached. The solution is n into a weighing bottle, and weighed; after which the of solid in solution is determined in a suitable manner.

more accurate determinations of the solubility, especially e solvent is appreciably volatile at the temperature of ex- t, other methods are preferable. In Fig. 115 is shown the us employed by H. Goldschmidt,[1] and used to a considerable n the laboratory of van't Hoff. This consists essentially of rts: *a*, a tube in which the solvent and salt are placed; losed at the foot by an india-rubber stopper. Through this there passes the bent tube *cb*, which connects the tube *a* weighing-tube *d*. At *c* there is a plug of cotton wool. is open to the air. The wider portion of the tube *cb*, which hrough the rubber stopper in *a*, can be closed by a plug attached to a glass rod *ff*, which passes up through a hollow Witt stirrer, *g*. After being fitted together, the whole apparatus is immersed in the thermostat. After the solution has become saturated, the stopper of the bent tube is raised by means of the rod *ff* and a suction-pump attached to the end of *e*. The solution is thereby drawn into the weighing-tube *d*, the undissolved salt being retained by the plug at *c*. The apparatus is then removed from the thermostat, tube *d* detached and immediately closed by a ground stopper. It is then carefully dried and weighed.

---

[1] *Zeitschr. physikal. Chem.*, 1895, 17. 153.

Another form of solubility vessel, due to Meyerhoffer and Saunders, is shown in Fig. 116.[1] This consists of a single tube, and the stirring is effected by means of a glass screw.

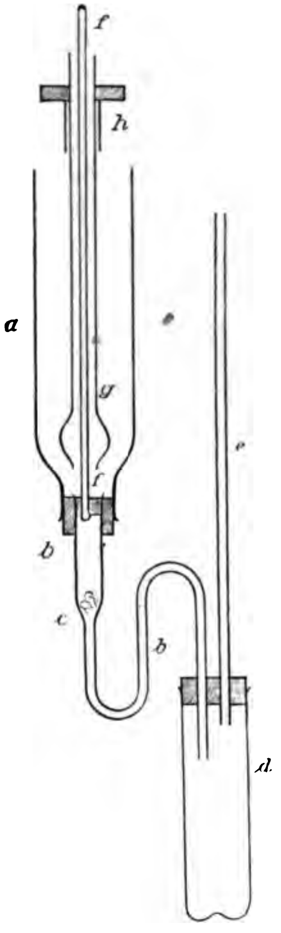

FIG. 115.

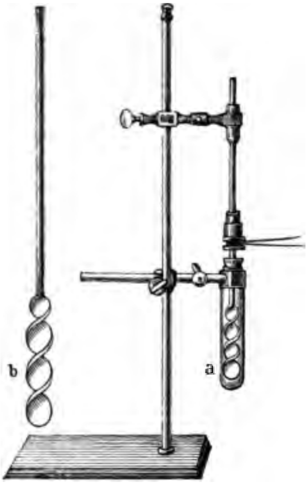

FIG. 116.

The progress of the solution towards saturation can be very well tested by determining the density of the solution from time to time. This is most conveniently carried out by means of the pipette shown in Fig. 117.[1] With this pipette the solution can not only be removed for weighing, but the volume can be determined at the same time. It consists of the wide tube *a*, to which the graduated capillary *b*, furnished with a cap *c*, is attached. To the lower end of the pipette the tube *e*, with plug of cotton wool, can be fixed. After the pipette has been filled by sucking at the end of *b*, the stop-cock *d* is closed and the cap *c* placed on the capillary. The apparatus can then be weighed, and the volume of the solution be ascertained by means of the graduations.

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[1] *Zeitschr. physikal. Chem.*, 1899, 28. 464.

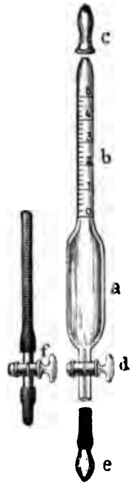

FIG. 117.

As has already been insisted, particular care must be paid to the characterization of the solid in contact with the solution.

IV. Thermometric Method.—If a substance is heated, its temperature will gradually rise until the melting point is reached, and the temperature will then remain constant until all the solid has passed into liquid. Similarly, if a substance which can undergo transformation is heated, the temperature will rise until the transition point is reached, and will then remain constant until complete transformation has taken place.

This method, it will be remembered, was employed by Richards for the determination of the transition point of sodium sulphate decahydrate (p. 134). The following figures give the results obtained by Meyerhoffer in the case of the transformation :—

$$CuK_2Cl_4,2H_2O \rightleftarrows CuKCl_3 + KCl + 2H_2O$$

the temperature being noted from minute to minute : 95°, 93°, 91·8°, 91·7°, 92°, 92·3°, 92·4°, 92·2°, 92·2°, 92°, 90·5°, 89°, and then a rapid fall in the temperature. From this we see that the transition point is about 92·2°. It is also evident that a slight supercooling took place (91·7°), owing to a delay in the transformation, but that then the temperature rose to the transition point. This is analogous to the supercooling of a liquid.

A similar halt in the temperature would be observed on passing from lower to higher temperatures ; but owing to a lag in the transformation, the same temperature is not always obtained.

---

[1] Meyerhoffer and Saunders, *ibid.*, p. 466.

V. Optical Method.—The transition point can sometimes be determined by noting the temperature at which some alteration in the appearance of the substance occurs, such as a change of colour or of the crystalline form. Thus mercuric iodide changes colour from red to yellow, and the blue quadratic crystals of copper calcium acetate change, on passing the transition point, into green rhombs of copper acetate and white needles of calcium acetate (p. 252). Or again, changes in the double refraction of the crystals may be also employed to ascertain the temperature of the transition point. These changes are best observed by means of a microscope.

For the purpose of regulating the temperature of the substance a small copper air-bath is employed.[1]

VI. Electrical Methods.—Electrical methods for the determination of the transition point are of two kinds, based on measurements of conductivity or of electromotive force. Both methods are restricted in their application, but where applicable give very exact results.

The former method, which has been employed in several cases, need not be described here. The second method, however, is of considerable interest and importance, and calls for special reference.[2]

If two pieces, say, of zinc, connected together by a conducting wire, are placed in a solution of a zinc salt, *e.g.* zinc sulphate, the potential of the two electrodes will be the same, and no current will be produced in the connecting wire. If, however, the zinc electrodes are immersed in two solutions of *different* concentration contained in separate vessels, but placed in connection with one another by means of a bent tube filled with a conducting solution, the potentials at the electrodes will no longer be the same, and a current will now flow through the connecting wire. The direction of this current *in the cell* will be from the weaker to the more concentrated solution.

The greater the difference in the concentration of the solutions with respect to zinc, the greater will be the difference of the potential at the two electrodes, or the greater will be the E.M.F. of the cell. When the concentration of the two solutions becomes the same, the E.M.F. will become zero, and no current will pass.

It will be understood now how this method can be made use of

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[1] See Van Eyk, *Zeitschr. physikal. Chem.*, 1899, **30**. 446.

[2] See in this connection the volume in this series on *Electro-chemistry*, by Dr. R. A. Lehfeldt.

:rmining the transition point of a salt, when we bear in ıat at the transition point the solubility of the two forms s identical. Thus, for example, the transition point of zinc e heptahydrate into hexahydrate could be determined in the ıg manner. Tube A (Fig. 118) contains, say, a saturated ı of the heptahydrate along with some of the solid salt; tube :urated solution of the hexahydrate along with the solid salt. ›e C is a connecting tube bent downwards so as to prevent :ing of the solutions by convection currents. ZZ are two zinc les immersed in the solution; the cell is placed in a ther- and the zinc electrodes connected with a galvanometer. ıow, at temperatures below the transition point the solubility ıexahydrate (the metastable form) is greater than that of the

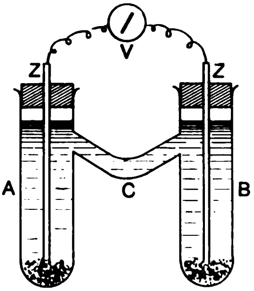

FIG. 118.

ydrate, a current will be produced, flowing in the cell from ydrate to hexahydrate. As the temperature is raised s the transition point, the solubilities of the two hydrates proach, and the current produced will therefore become , because the difference in the E.M.F. of the cell becomes ınd when the transition point is attained, the E.M.F. ꞩs zero, and the current ceases. If the temperature is above this, the solubility of the heptahydrate becomes than that of the hexahydrate, and a current will again be ed, but in the opposite direction. By noting the tempera- erefore, at which the current ceases, or the E.M.F. becomes ıe transition temperature can be ascertained.

:he case just described, the electrodes consisted of the same ıs was contained in the salt. But in some cases, *e.g.* sodium :e, electrodes of the metal contained in the salt cannot be 'ed. Nevertheless, the above electrical method can be used even in those cases, if a suitable non-polarizable mercury electrode is employed.[1]

Although, as we saw, no current was produced when two pieces of zinc were immersed in the same solution of zinc salt, a current will be obtained if two different metals, or even two different modifications of the same metal, are employed. Thus an E.M.F. will be established when electrodes of grey and of white tin are immersed in the same solution of zinc salt, but at the transition point this E.M.F. will become zero. By this method Cohen determined the transition point of grey and white tin (p. 40).

---

[1] For a description and explanation of these, the reader should consult the volume in this series by Dr. Lehfeldt on *Electro-chemistry*; and van't Hoff, *Bildung und Spaltung von Doppelsalzen*, p. 48 *ff*.

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